

On the sensitiveness of photographic dry plates.

By

Michio Miyata.

(Received March 17, 1930.)

CONTENTS.

(I) Visible darkening of silver halide crystals by the action of light.....	115
(II) Impurities in the precipitate of AgBr.....	118
(III) Precipitation of AgCl together with AgBr.....	119
(A) Method of titration.	121
(B) Experiments for the case of dilute solution.	122
(C) Influence of the concentration of both halides at the equal molar concentration ratio.	123
(D) Experiments for the case of concentrated solution.	125
(E) Mechanism of AgCl precipitation in AgBr.	125
(F) Function of barium nitrate.	130
(IV) Precipitation of AgCl in AgBr of dry plates.	132
(A) Chloride in commercial potassium bromide as an impurity.	132
(B) Influence of the conditions under which AgBr emulsion are prepared. ...	133
(V) Chemical analysis of AgBr emulsions.	137
(A) Soluble halides in AgBr emulsions.....	138
(B) Silver halides in AgBr emulsions.	139
(IV) AgCl as sensitive nuclei.	141
(A) AgCl as sensitive specks in the visible darkening of AgBr.	141
(B) Behaviour of AgCl in AgBr emulsions.	142
(C) AgCl nuclei plates.....	143
(D) Emulsion containing two kinds of silver halides.....	145
(E) Visible darkening of the mixture of silver halides.....	147
(VII) Formation of emulsions and the AgCl nuclei.....	152
(A) Action of gelatin in emulsions.	152
(B) Ripening of emulsions.	158
(C) Nature of fog.	162
(D) Action of AgI.	164
(E) Experiments showing some features of the formation of emulsions.....	165
(VIII) Properties of AgBr gelatin emulsions.	170
(A) Developability of AgBr grains.	171
(B) Sensitivity and size of AgBr grains.	173
(C) Spectral sensitivity of AgBr emulsions.	174
(D) Why is AgBr used in dry plates?	176
Summary.	177

ON THE SENSITIVENESS OF PHOTOGRAPHIC DRY PLATES.

Compared with the many other photo-chemical changes which occur in nature or are secured by artificial methods, the change produced in photographic dry plates by the action of light is so wonderfully rapid that any one would easily suppose that the mechanism of this change is extremely different from that in other substances.

But little fundamental to the explanation of the sensitiveness of photographic dry plates has yet been achieved. In fact, among the many subjects which have a wide application to science and industry, there is probably none which is so little understood as that of photography.

For these reasons, the excellence of modern dry plates is due rather to the application of laboriously acquired empirical knowledge than to that of scientific principles. But the discovery of the development centres⁽¹⁾ in the silver bromide grains of photographic dry plates has opened a new field for the investigation of the characteristic nature of the sensitiveness of highly sensitive dry plates though it has little connection with the primary change which occurs generally by the action of light and it is fairly well agreed⁽²⁾ at the present time that these development centers are formed at preexisting sensitive points consisting of some other material than silver bromide, which are called generally sensitive nuclei.

What is the nature of these sensitive nuclei?

This is the final question, attained as the result of numerous investigations during the fifty years that have elapsed since dry plates were introduced, and this question has vital importance for photographic theories and the photographic industry, touching the very heart of the mystery of photography.

The colloid silver theory of Renwick⁽³⁾ and the silver sulphide theory

(1) Bancroft: *Trans. Faraday Soc.*, **19** 243 (1923).

Svedberg: *Phot. Jour.* **62** 183 (1922).

(2) Sheppard: *Trans. Faraday Soc.*, **19** 309 (1923).

(3) *Brit. J. Phot.*, **67** 447, 463 (1920).

of Sheppard⁽⁴⁾ have eminently explained this problem and given a valuable idea of the sensitive nuclei. But the present author intends to give another explanation on this problem in the following manner :

(I) VISIBLE DARKENING OF SILVER HALIDE CRYSTALS BY THE ACTION OF LIGHT.

Several reseaches of this kind have already been published but in most of them the amorphous silver halides are treated as homogeneous substances and not many investigations on the individual crystal of them are to be found. But, as the function of silver halides in photographic dry plates is the sum of the results which appear from individual crystals of them, it is rather interesting to observe the visible darkening of single crystals. R. Lorenz⁽⁵⁾ has found that crystals of AgCl or AgBr, prepared in the ordinary way and exposed to light in an ultramicroscope, show innumerable particles, which are believed by him to be metallic silver formed by the decomposition of silver halides themselves by light. Trivelli⁽⁶⁾ and Trivelli & Sheppard⁽⁷⁾ studied the visible darkening of AgBr grains in gelatin emulsions with an ordinary microscope. In the present experiment, the object was to learn the general features of the visible darkening which occurs in the crystal of AgCl, AgBr or AgI, prepared from aqueous solutions, both with the ultramicroscope and with the ordinary microscope. The crystals of these kinds of silver halides were precipitated first by mixing 20 c.c. of potassium halide solution (1.0 mol/litre) and 10 c.c. of AgNO₃ solution (1.0 mol/litre). The precipitate of AgCl or AgBr was suspended, after washing, in dilute ammonia (0.880 × 10) and that of AgI in KI solution (1.0 mol/litre) and then they were recrystallized by suitable digestion in the form of thin crystabls. Such crystals were prepared as microscopic slides, Canada balsam being used as the filling medium. The objective of the microscope which carries an iris diaphragm was used both for the purpose of dark ground observation and

(4) Phot. J. **49** 380 (1925).

(5) Z. anorg. Chem., **91** 46, 56, 61 (1915).

(6) AgBr grains in photo. emulsion. (1921) p. 110.

(7) J. phys. Chem., **29** 1568 (1925).

for ordinary observation by transmitted light, its N.A. varying from 0.8 to 1.25. As the substage condenser a Zeiss "Wechsel-Kondensor" was used, which can be used for any of the above two observations. By regulating such an objective and condenser, any of these observations can be made in case of necessity. The microscope was illuminated by an arc-lamp (5.0 Amp) continuously and on observing the change at frequent intervals both ultramicroscopically and with the ordinary microscope, the time in which the crystal got a definite change with any one of the illuminations was recorded. The results of the observations are shown in Table 1. and the photomicrographs ($\times 1100$) by dark ground illumination in Fig. 1—3.

Table 1.

Silver halide	AgCl		AgBr		AgI	
	Transmitted	Dark ground	Transmitted	Dark ground	Transmitted	Dark ground
1st. observation	Transparent	bright points on whole surface	Transparent	Transparent	Transparent	Transparent
2nd. observation	after 5 mins.		after 3 mins.		after 120 mins.	
	slight coloring	bright points on whole surface	a few colored spots	a few bright spots	bright points	bright points
3rd. observation	after 10 mins.		after 8 mins.		after 360 mins.	
	more coloring	bright points on whole surface	a few colored spots	a few bright spots	bright points	bright points
4th. observation	after 15 mins.		after 68 mins.		after 750 mins.	
	strong coloring	bright points on whole surface	more colored spots	more bright spots and bright points on whole surface	more bright points	more bright points

From the results of these observations, it is definitely known that not only are there inequalities of sensitivity in these three silver halides, but also there are noticeable differences in their manners of visible darkening.

Silver chloride is seen to darken uniformly when observed with the ordinary microscope and the change in it can be merely resolved after a fairly long exposure into minute, dense and bright points by the ultramicroscope. Hence, the change in AgCl may be considered rather to be a uniform one in its whole surface. Silver bromide changes quite in another way, that is to say, at the earliest stage of change, it shows a few spots both with the ultramicroscope and with the ordinary microscope and on continuing its exposure to light, the change spreads only around the above spots at a certain period and the increase in the number of the spots is very little. After very long exposure to light, it changes at last uniformly just as AgCl changes in the early stage. Thus the change in AgBr in the early stage can not be considered as its own change, but the spots that appear in this stage are to be regarded as coming from specks consisting of some foreign substance which exists as an impurity in AgBr.

But the change in AgBr in the later stage seems to be its own one. Silver iodide changes in a similar manner to silver chloride but in a much longer time, though it shows in rare cases one or two spots in a crystal as in all cases of silver bromide.

Hence, only the visible change in silver bromide in the early stage differs distinctly from that of silver chloride or silver iodide and closely resembles the change in silver bromide grains in gelatin emulsions at the formation of development centres during their development.

The remarkable point in the above results of observation is first that the formation of special spots in the visible change of silver bromide crystals occurs in crystals which were precipitated from an aqueous solution and the manner of the occurrence of such special spots by light closely resembles that of development centres in development.

From these results, the origin of the spots which appeared in the visible darkening of AgBr crystals seems to be the same as that of the sensitive nuclei in AgBr grains of photographic emulsions. Thus, the sensitive nuclei of AgBr grains may be presumed to originate at the precipitation of AgBr, their origin being some foreign substance which accompanies the precipitants of AgBr as an impurity.

Accordingly, some of the theories in which the origin of the sensitive nuclei is attributed only to the action of gelatin may be said to be doubtful.

Secondly, it is noticeable that the time taken for the formation of the spots in AgBr crystals is about equal to that for the change of the whole surface of AgCl crystals. This fact gives some idea that the origin of the sensitive nuclei in AgBr grains may be the AgCl which was occluded at their precipitation.

Thirdly, some collapse in the structure of silver halide crystals is found after a long exposure to light which may be considered to be due to the pressure of halogen gas produced within the crystal by the action of light. (See Fig. 2, No. 4.)

In brief, it is known that the change produced in AgBr by the action of light is quite different in its features to that of AgCl or AgI and the source of the sensitive nuclei is present at precipitation even from aqueous solutions.

(II) IMPURITIES IN THE PRECIPITATE OF AgBr.

In the preceding section, it was found that the AgBr crystal precipitated from an aqueous solution has always specially sensitive specks and they were considered to be some foreign substance contained therein as an impurity. But the AgBr crystal which was examined with the microscope was obtained only from "Merck's pure chemicals". Hence, it is by no means easy to find the nature of the impurity by any ordinary means of chemical analysis, since its existence was detected only by means of the photochemical decomposition, which seems to be more sensitive than ordinary chemical analysis. Therefore, there is nothing for it but to investigate the impurity by some other indirect means. Here, as interesting facts having a bearing on this problem, the following may be stated:

1. In the analytical chemistry, it is well known that, when AgNO₃ solution is added to a mixture of KBr solution and KCl solution a trace of AgCl precipitates together with AgBr before the total KBr is precipitated as AgBr⁽⁸⁾.

(8) Fehling: Jour. prakt. chem., 45 269 (1878).

2. In commercial KBr which is used for the precipitation of the AgBr of photographic dry plates, some small amount of soluble chloride is always contained (this fact will be shown later by an analytical result).

Taking these two facts into consideration, it may be considered that a very small amount of AgCl is present in the AgBr precipitate of dry plates.

But it must be added that the silver halides are generally believed⁽⁹⁾ to precipitate exactly in the order of their solubility when AgNO₃ solution is added to the solution of KI, KBr and KCl, at their fractional precipitation; that is, after all the KI has precipitated as AgI completely, AgBr begins to precipitate and when the precipitation of AgBr is complete, AgCl precipitates finally. Thus the precipitation of two kinds of silver halides at the same time is said to be quite impossible. At the precipitation of AgBr for dry plates, an excessive amount of alkali bromide for AgNO₃ is always taken. Accordingly, from the idea above mentioned, it is quite impossible that a small amount of AgCl should be present in the precipitate of AgBr even in the case of some small amount of alkali chloride being contained as an impurity in alkali bromide.

But it may be easily supposed that at the precipitation of insoluble or hardly soluble substances, the phenomenon of the formation of a solid substance is very complicated and the ordinary chemical law may fail at some points. So even in the above case, it may be impossible to deny simply the precipitation of AgCl in the precipitate of AgBr.

(III) PRECIPITATION OF AgCl TOGETHER WITH AgBr.

When AgNO₃ solution is added to the mixed solution of KCl and KBr, theoretically the precipitation of pure AgBr must occur before AgCl begins to precipitate because the solubility of AgBr is much less than that of AgCl. But as the matter of fact, it has been recognized by Fehling⁽⁸⁾ that precipitation of AgCl accompanies the early stage of the precipitation of AgBr. Küster⁽¹⁰⁾, investigating this phenomenon, in which the ordinary

(9) Rose: *Handb. analy. Chem.*, **2** 574.

(10) *Z. anorg. Chem.*, **19** 81 (1899).

chemical law fails, says that it is due to the formation of a solid solution of these two silver halides.

Whatever the case may be, this fact has proved troublesome in the quantitative determination of chlorine and bromine by the electrometric titration. According to Dutoit and Weisse⁽¹¹⁾, the quantitative separation of these two is impossible even by this electrometric method, but Liebig⁽¹²⁾ obtained a successful result by mixing barium nitrate with the titrating solution up to the amount of 5%. Following Liebig's proposal, Müller⁽¹³⁾ obtained the results shown in Table 2.

Table 2.
Müller's result.

Composition of the solutions titrated.				Results of titration (mol%)	
0.1 KBr c.c.	0.1 KCl c.c.	$\frac{\text{KCl}}{\text{KBr}}$ mol ratio	water added c.c.	$\frac{\text{AgCl}}{\text{AgBr}}$ (with Ba)	$\frac{\text{AgCl}}{\text{AgBr}}$ (no Ba)
0.25	10.0	40.0	159.75	36.0	16.0
0.50	10.0	20.0	159.50	16.0	0.0
2.0	10.0	5.0	158.00	17.0	2.5
5.0	10.0	2.0	155.00	9.8	2.8
10.0	10.0	1.0	150.00	7.9	1.2
10.0	5.0	0.5	155.00	—	1.0
10.0	2.0	0.2	158.00	0.2	0.2
10.0	0.5	0.05	159.50	1.2	0.2
10.0	0.25	0.025	159.75	5.4	0.0
10.0	0.125	0.0125	159.875	11.1	-0.4

The result in Table 2 was obtained by titrating with 0.1 AgNO₃ solution (the unit of concentration is mol per litre, and hereafter the same unit will be used throughout the present paper), a calomel electrode and silver wire being taken as the titrating electrodes. The molar percentage of AgCl to AgBr in the result of titration was calculated from the end point of bromine titration, which was found to be excessive with regard to

(11) J. chim. Phys., 9 578 (1911).

(12) Müller: Elektromassanalyse., 4 Aufl. (1926) p. 99.

(13) Müller: Elektromassanalyse., 4 Aufl. (1926) p. 104.

the actual amount of KBr taken in the titrating solution. This result Müller explains from the standpoint of analytical separation as follows:

“In the case in which the molar concentration of the two is equal, the deviation of the bromine end is unavoidably 10.0% even when there is some amount of barium nitrate present. This deviation becomes smaller as the amount of Cl decreases but the deviation is not smaller than 0.2% till the ratio of molar concentration becomes Br 5 : Cl 1. Hence, this method of titration can not be used for the quantitative separation unless the concentration ratio is less than this.

The diminution of deviation by the addition of barium nitrate depends most likely on the limitation of the formation of a solid solution of AgBr and AgCl by the action of barium nitrate.”

Whatever the cause of the deviation may be, it is clear from this result of Müller's that AgCl precipitates together with AgBr. But it is still open to question whether the same phenomenon occurs in the preparation of AgBr emulsion for photographic dry plates. The present author examined this problem in detail in the following manner:

(A) Method of titration.

For the precipitation of AgBr, AgNO₃ solution was added drop by drop from a burette to KBr solution which was agitated with a motor, the speed of which properly regulated by a resistance. The electrodes for the determination of the electromotive force in the titrating solution were the same as those of Müller's and they were connected to the “Hydrogen ion Potentiometer” and galvanometer of Leeds and Northrup.

The approach of the titration to the Br end point is to be known from the rate of change of E.M.F. in response to the addition of unit volume of AgNO₃. From this stage of titration, AgNO₃ solution was added only one drop at a time and the solution was agitated at least five mins. and after the settling of E.M.F. was ascertained the next drop was added and so on. The end point of titration was determined when the jump of E.M.F. in response to two consecutive drops of AgNO₃ was greatest. Thus the Br end point appears at first and the end point for the

sum of Br and Cl appears secondly after the addition of some more AgNO_3 solution. The molar percentage of AgCl which precipitated together with AgBr , was calculated from the difference between the mols of AgNO_3 used for the Br end point and the actual mols of KBr mixed originally with the titrating solution.

No matter what the conditions of titration or the composition of the titrating solution may be, the total end point for Br and Cl always coincides with the actual sum of the two, which were previously standardized separately. Hence it is not necessary to determine the total end point at every titration and the excess of Br at its end point over that of actual Br can be taken as the amount of Cl which precipitated together with Br. The water used throughout for this experiment was triple distilled one, all the chemicals were Merck's and the temperature of the solutions was 16—20°C.

(B) Experiments for the case of dilute solutions.

As a preliminary experiment, the following shown in Table 3, was carried out with the idea of testing Müller's result.

Every titrating solution was diluted with water up to 200 c.c. on one hand and on the other hand 10 g of barium nitrate was dissolved in every titrating solution, which was diluted up to the same volume. The concentration of AgNO_3 solution used for every titration was 0.1 mol per litre.

Table 3.

Composition of the solutions titrated			Results of titration (mol %)		
0.1 KBr c.c.	0.1 KCl c.c.	$\frac{\text{KCl}}{\text{KBr}}$ mol ratio	$\frac{\text{AgCl}}{\text{AgBr}}$ (no Ba)	$\frac{\text{AgCl}}{\text{AgBr}}$ (Ba before just end)	$\frac{\text{AgCl}}{\text{AgBr}}$ (Ba from beginning)
20.0	40.0	2.0	13.09	3.09	1.34
20.0	20.0	1.0	20.09	2.57	1.34
20.0	10.0	0.5	10.34	1.57	0.87
20.0	5.0	0.25	8.34	1.22	0.67
20.0	2.0	0.10	4.17	0.98	0.50
20.0	1.0	0.05	2.50	0.67	0.34
20.0	0.5	0.025	1.09	0.00	0.17
20.0	0.2	0.010	0.00	0.00	0.09
20.0	0.1	0.005	-0.02	-0.17	0.09

The results resemble on the whole those of Müller's, but the percentage of AgCl which precipitated together with AgBr is somewhat smaller than that obtained by Müller. The difference in the results may be considered to be due probably to the degree of agitation in the course of titration, especially in the neighbourhood of the Br end. From this result, just as from Müller's, it is known that the greater the molar concentration ratio of KCl to KBr, the greater is the percentage of AgCl which precipitates together with AgBr, and a great difference appears when barium nitrate is present.

Here, the time at which the barium nitrate was added was divided into two cases, namely in one case the barium was added at the beginning of titration and in the other case, it was added just before the end point. The experimental values in the latter case are generally a little larger and therefore barium nitrate is considered to act at every moment when the precipitation occurs. As to the cause of the different results according to the compositions of the solutions, Müller attributed it in his conclusion only to the molar concentration ratio of the two halides in the titrating solution. But if we observe the composition of the titrating solution both in Table 2 and in Table 3, the variation is not only in the molar concentration ratio but also in the concentration of the individual halides in both cases, because the volume of every titrating mixture was always equal. Accordingly, it will be ascertained in the next section whether the variation in the experimental result is due only to the molar concentration ratio or is connected with the concentration of each component itself.

(C) The influence of the concentration of both halides at equal molar concentration ratio.

As is seen in Table 3, the experimental value obtained with no barium is very large and this may be connected with some experimental error as stated in a later section. In this experiment, therefore, that case was omitted and only the case where barium nitrate was present was examined. The amount of barium nitrate was taken so as to make it

5.0% in every titrating solution according to its volume. The other conditions were quite the same as in Table 3 and the result is shown in Table 4.

Table 4.

Compositon of the solutions titrated.				Results (mol %)
o.1 KBr c.c.	o.1 KCl c.c.	$\frac{\text{KCl}}{\text{KBr}}$ mol ratio	diluted with water up to, c.c.	$\frac{\text{AgCl}}{\text{AgBr}}$ (with Ba)
20.0	20.0	1.0	25	1.84
20.0	20.0	1.0	50	1.34
20.0	20.0	1.0	100	1.09
20.0	20.0	1.0	200	1.84
20.0	20.0	1.0	400	0.50
20.0	2.0	0.1	100	0.67
20.0	2.0	0.1	200	0.67
20.0	2.0	0.1	400	0.42
20.0	2.0	0.1	800	0.00

In this experiment, the molar concentration ratio in every titrating solution was kept always equal, its dilution being varied so as to vary only the concentration of individual halides. As is seen in Table 4, in the case of both molar ratio 1.0 and 0.1, marked differences are found even according to the difference in the concentration of individual halides. Hence it is impossible to attribute the variation in the experimental results only to the difference in the molar ratio, but it must be taken into consideration that even with the same molar ratio a great difference appears according to the dilution of the titrating solution. From the standpoint of quantitative analysis in the case of the mixture of Br and Cl, it may be said that better results will be obtained by a suitable dilution of the titrating solution even with a sample of the same molar ratio. On the other hand, if it is necessary to increase the amount of AgCl which precipitates together with AgBr, the concentration of Br and Cl must be taken suitably large.

(D) Experiments for the case of concentrated solution.

In the above experiment, it was found to be impossible to disregard the concentration of individual halides even when the molar ratio of the two halides remains equal. In the precipitation of AgBr for photographic dry plates, the concentration of KBr is generally very large.

Hence, with reference to that case, the influence of the molar ratio of the two halides was obtained for the case of concentrated titrating solutions. The concentration of every titrating solution was 0.5 mol per litre and that of AgNO₃ was 1.0 mol per litre. The result both for solutions with 5.0% of barium and for solutions with no barium are shown in the following table (Table 5):

Table 5.

Composition of the solutions titrated.				Results (mol %)	
1.0 KBr c.c.	1.0 KCl c.c.	$\frac{\text{KCl}}{\text{KBr}}$ mol ratio	water added c.c.	$\frac{\text{AgCl}}{\text{AgBr}}$ (no Ba)	$\frac{\text{AgCl}}{\text{AgBr}}$ (with Ba)
20.0	20.0	1.0	0.0	1.5	1.9
20.0	10.0	0.5	10.0	1.5	1.9
20.0	5.0	0.25	15.0	1.0	1.4
20.0	2.0	0.10	18.0	0.75	1.09
20.0	1.0	0.05	19.0	0.44	0.53
20.0	5.0 (0.1 KCl)	0.025	15.0	0.13	0.34
20.0	2.0 (")	0.010	18.0	0.09	0.09
20.0	1.0 (")	0.005	19.0	0.00	0.00

According to these results, the influence of barium on the experimental value is reversed when compared with that in the case of dilute solutions, that is, in the case of the titration with barium, the percentage of AgCl which precipitates together with AgBr is a little larger than that in the case with no barium.

Thus the influence of barium is quite reversed according to the concentration of the titrating solution.

(E) The mechanism of AgCl precipitation in AgBr.

In spite of the fact that the solubility of AgCl is about ten times

greater than that of AgBr, why does AgCl precipitate in the presence of free Br ions? As the mechanism of the precipitation of AgCl in this case has an important significance in the formation and the properties of photographic emulsions, the following additional experiments were made to find some explanation for it:

(a) The result shown in Table 3 shows the influence of the concentration of KCl on the amount of AgCl which precipitates together with AgBr, the concentration of KBr remaining constant. And the result shown in Table 4 gives the influence of the concentration of the two halides. In this experiment, the influence of the concentration of KBr was examined, the concentration of KCl being taken constant. Each solution of the mixture of KBr and KCl, which was diluted with water up to 200 c.c. and in which 10 g of barium nitrate was dissolved, was titrated with a solution of 0.1 AgNO₃. The result is shown in Table 6.

Table 6.

Composition of the solutions titrated.			Results (mol %)	From Table 3.
0.1 KBr c.c.	0.1 KCl c.c.	$\frac{\text{KCl}}{\text{KBr}}$ mol ratio.	$\frac{\text{AgCl}}{\text{AgBr}}$	$\frac{\text{AgCl}}{\text{AgBr}}$
2.0	2.0	1.0	2.50	1.34
4.0	2.0	0.5	2.18	0.87
8.0	2.0	0.25	1.85	0.67
20.0	2.0	0.10	0.50	0.50
40.0	2.0	0.05	0.00	0.34

It is known from this result that when the concentration of KBr is greater, the percentage of AgCl precipitation is less, which result is contrary to that obtained with KCl. The formation of AgCl in AgBr seems to be reduced in concentrated solutions of KBr.

(b) According to Liebig, the optimum concentration of barium nitrate in the titrating solution is 5.0% and Müller also obtained the result shown in Table 2, with this concentration of barium nitrate.

In this experiment, the influence of the concentration of barium nitrate was examined and also that of calcium nitrate, which has similar

property to barium nitrate in some points. The results are shown in Table 7.

Table 7.

Composition of the solutions titrated.				Results of titration (mol %)	
0.1 KBr c.c.	0.1 KCl c.c.	Ba or Ca added c.c.	mol concentra- tion of Ba or Ca. c.c.	$\frac{\text{AgCl}}{\text{AgBr}}$ (with Ba)	$\frac{\text{AgCl}}{\text{AgBr}}$ (with Ca)
20.0	1.0	1.0	0.005	0.13	—
20.0	1.0	2.0	0.01	0.13	0.32
20.0	1.0	4.0	0.02	0.13	0.13
20.0	1.0	8.0	0.04	0.13	0.13
20.0	1.0	20.0	0.10	0.23	—
20.0	1.0	40.0	0.20	0.32	—

The results show that the influence of the concentration of barium nitrate does not vary very much in its wide range and the action of calcium nitrate is not different from that of barium nitrate.

Thus, it is known that some divalent ions seem to have a similar action and if the condition of the precipitates in the course of titration is observed, it will be found that these divalent ions cause the strong coagulation of the precipitate. Taking these facts into consideration, the action of these divalent ions on the result of titration seems to be related to the coagulation itself of the precipitates.

(c) In many cases, the time required for the mixing of two solutions to get precipitates has a remarkable influence on the nature of the precipitate. In this experiment, this point was examined in the precipitation of AgBr and AgCl. Each solution to be titrated was diluted with water up to 200 c.c. and was titrated with solution of 0.1 AgNO₃, the time taken to mix the two solutions being varied as shown in Table 8. In the case of the shortest time (1 sec.), the main part of the AgNO₃ solution was added at once from a beaker and then it was titrated from a burette drop by drop. The main part of the AgNO₃ solution was measured by weighing the beaker before and after the pouring out of the solution. In other cases, the time was regulated by the cock of the burette. The result is shown in Table 8.

Table 8.

Solutions titrated.		Time occupied for mixing 20 c.c. 0.1 AgNO ₃ .	Results of titration with Ba. (mol %.)
0.1 KBr c.c.	0.1 KCl c.c.		
20.0	1.0	1.0 sec.	0.50
20.0	1.0	65.0 "	0.32
20.0	1.0	8.0 mins.	0.13
20.0	1.0	60.0 "	0.00

The influence of time is to be seen though it is not large. And it is remarkable in this result that if the time required for mixing is chosen suitably long, the precipitation of AgCl together with AgBr practically does not occur. But it must be remembered that this result was obtained only in the case of dilute solutions containing barium nitrate.

(d) The precipitation of AgCl together with AgBr is only ascertained, as it was already described, by the deviation of Br end from the actual amount of Br in solution. Hence, it is not yet determined whether every small amount of AgCl precipitates at every moment of the precipitation of AgBr, or whether it precipitates after the precipitation of all the AgBr and the maximum jump of E.M.F. appears owing to some influence of the AgBr already precipitated.

To decide this question, the following experiment was made. In this test, KCl solution was mixed with KBr solution at a certain stage in the course of titration after some of the titration for pure KBr solution has been finished. The other conditions of the titration were quite the same as the foregoing ones. The result is shown in Table 9.

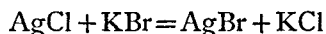
Table 9.

Solutions titrated.			Vol of KBr titrated with no KCl c.c.	Vol of KBr titrated with KCl c.c.	Results of titration with Ba. (mol %)
0.1 KBr c.c.	0.1 AgNO ₃ c.c.	0.1 KCl c.c.			
20.0	0.0	20.0	0.0	20.0	0.50
20.0	5.0	20.0	5.0	15.0	0.50
20.0	10.0	20.0	10.0	10.0	0.50
20.0	15.0	20.0	15.0	5.0	0.32
20.0	19.8	20.0	19.8	0.2	0.00

The result shows that the precipitation of AgCl does not occur if KCl is added shortly before the end point of Br, and that if KCl is present from the earlier stage of titration, AgCl seems to precipitate at every moment of AgBr precipitation. In other words, AgCl precipitates already in the presence of KBr.

(e) Explanation. From these results, the mechanism of the precipitation of AgCl together with AgBr may be explained as follows:

When one drop of AgNO₃ solution (B solution) is poured into the titrating solution (A solution) which contains KBr and a little KCl, AgNO₃ will react mainly with KBr at once but some small part of B solution will certainly react with KCl because there exists some small amount of KCl in the boundary surface between the drop of B solution and A solution. At the moment of such precipitation, at least two parallel phenomena will occur; the one phenomenon is the rapid coagulation of primary particles of silver halides by the influence of electrolyte which exists in the solution, and the other one is the double decomposition between AgCl and KBr as follows:



The former change will depend on the reacting concentration of the A and B solutions but this will be much reduced by the rapid agitation which dilutes the density of the primary particles. The latter change is much accelerated by the agitation which provides an opportunity for AgCl and KBr to come in contact. Thus these two changes, the rapid coagulation and the double decomposition will occur in any order according to the conditions of precipitation. If the latter change occurs completely before the former begins, the secondary aggregate will be formed only from pure AgBr.

On the other hand, if the former occurs rapidly before the latter is completed, the secondary aggregate will be formed from AgBr and AgCl.

In the secondary particles formed by such rapid coagulation of AgBr and AgCl, some AgCl will be covered completely by AgBr. It is well known⁽¹⁴⁾ that such secondary particles are often so strongly combined that

(14) Svedberg: *Colloid chemistry*, 2nd Ed. (1928) p. 252.

it is impossible to integrate again the secondary particles without destroying the primary particles themselves. The AgCl particles thus covered completely by AgBr particles within AgBr grains will be preserved without changing on further agitation to AgBr by the action of KBr. From this point of view, the influences of the molar ratio and the concentration of individual halides may be explained as follows:

In the case of larger molar ratio, the percentage of KCl which exists on the boundary surface of two solutions will be larger, and therefore the percentage of such occlusion of AgCl will be larger. In the case of greater concentration of the reacting solutions, the molar ratio remaining equal, the density of primary particles will be greater and the coagulation will be much accelerated by it and moreover, when the reacting concentration is greater, the velocity of coagulation is also accelerated because the concentration of the electrolyte, which causes the coagulation, is higher. In this way, the percentage of AgCl occlusion will be increased. On the other hand, if the rate of addition of B solution is reduced during agitation, the density of primary particles on each addition of the drop of B solution will be reduced by agitation before the rapid coagulation occurs and the double decomposition will precede the coagulation. Thus, the AgCl occlusion will be reduced in this case. In brief, the occlusion of AgCl in AgBr seems to be some phenomenon which occurs at the precipitation of the two substances at the same moment and it seems to be not necessary to explain the precipitation of AgCl in AgBr by the assumption that it is a nature of these silver halides to form a chemical or physical combination. But it is another question whether these two silver halides may form such a combination when they come into contact in their nascent state.

(F) **The function of Barium nitrate.**

In the case in which the reacting concentration is small and there is no barium present, the percentage of AgCl precipitation is extraordinarily great as shown in Table 3. But it is very doubtful whether the value obtained really denotes the actual amount of AgCl occlusion or whether it

contains some experimental error. When the mixture of KBr and KCl solution is titrated electrometrically, the total end point for the sum of Br and Cl denotes, as stated already, the actual sum exactly whatever the condition of titration may be, but at the Br end, the result always shows some more Br than its actual amount. What is the cause of such difference between the first and the second end point? If the conditions of precipitation at these two end points are compared, there can be found a great difference therein.

At the Br end, the end point is always determined in the colloidal state of AgBr which is stabilized by the action of Cl', but at the final end point, there are no more stabilizing ions and the precipitate coagulates completely showing the so called "Klar Punkt" of Lottermoser⁽¹⁵⁾.

Now, it is well known that the colloidal silver halide has the same action as the corresponding halogen ion, that is, it acts as a "colloidal electrolyte"⁽¹⁶⁾. Thus, at the true Br end, the colloidal AgBr which has already reacted with a corresponding amount of AgNO₃, may show the same influence on E.M.F. as if there remained some amount of Br'. In this way, the apparent Br end seems to appear a little later, owing to the action of colloidal AgBr than the actual end of Br.

Accordingly, the percentage of AgCl which is precipitated together with AgBr, in the case where there is no barium, will contain some experimental error caused by the action of colloidal AgBr. On the other hand, if barium exists in the titrating solution, this divalent ion shows a strong influence on the coagulation of colloidal AgBr in opposition to the stabilizing action of Cl', and it will reduce the experimental error above stated. In the case of concentrated reacting solutions, the precipitate coagulates even in the absence of barium because the electrolyte itself in the titrating solution acts as coagulating agent. Hence, the percentage of AgCl occlusion in such a case will be much smaller even in the absence of barium than that in the case of dilute reaction solutions. If barium is added to

(15) Alexander: *Colloid chemistry*, Vol. I. (1926) p. 670.

(16) *Z. angew. Chem.*, **39** 347 (1926).

the concentrated solution, the rapid coagulation is accelerated and the AgCl occlusion is increased by it, as shown in Table 5. In short, the action of barium seems to be to reduce the experimental error caused by colloidal particles in the case of dilute reacting solutions.

(IV) PRECIPITATION OF AgCl IN AgBr OF DRY PLATES.

In the preceding sections, it was ascertained that at the precipitation of AgBr it is possible for a small amount of AgCl to be occluded in AgBr when some amount of KCl is contained as an impurity in KBr. In this section, are given the results of the investigation to see whether this occurs also in the case of the preparation of AgBr emulsion for dry plates.

(A) Chloride in commercial potassium bromide as an impurity.

Before the precipitation of AgCl in AgBr emulsion is examined, it must first be ascertained whether there is any chloride in the commercial potassium or ammonium bromide which is used for the preparation of AgBr emulsion. The contamination of bromide by chloride is easily imaginable if it is considered that the natural source of bromide is always accompanied by some chloride and that it is difficult to separate these two absolutely as they have similar solubility. Three samples of commercial potassium bromide and two of ammonium bromide were examined for chloride by the electrometric method. Both kinds of bromide showed always 0.5—2.0 mol % of chloride, the percentage varying according to the time of delivery from the dealer. But bromide free from chloride was never found. Other materials for AgBr emulsion, including AgNO₃, photographic gelatin, potassium iodide and commercial ammonia were examined for chloride but none of them contained so much chloride as the bromide.

Therefore, the main part of the chloride which enters into the material used for AgBr emulsion is considered to come from bromide. Here it must be noted that some trace of Cl undoubtedly comes always from any of the materials, vessels or water used, even though an absolutely pure bromide is used, because absolutely Cl free materials seem not to be found commonly.

(B) Influence of the conditions under which AgBr emulsions are prepared.

In the above section, it was stated that commercial potassium or ammonium bromide always contains some amount of chloride. Taking this fact and the results of electrometric titration in the preceding sections into consideration, the existence of some AgCl in AgBr emulsion admits of no doubt. Therefore, the influence of the conditions under which AgBr emulsions are prepared, on the precipitation of AgCl, was now examined. As the potassium bromide for this purpose, only a mixture of Merck's KCl and KBr was used. The experiment was divided into two parts. The one was for dilute solutions and the other for concentrated solutions. The aim in the former was to obtain exact results and that in the latter to gain information as to what happens under conditions similar to the actual case of the preparation of emulsions.

(a) Influence of gelatin.

In the case of titration when gelatin is present, the measurement of E.M.F. is very difficult because in certain cases, it does not settle even with half an hour agitation. This seems to be due to the protecting action of gelatin, which disturbs the coagulation of colloidal AgBr and this colloidal AgBr, for the reason described in (III) (F), hinders the settling of E.M.F. In this experiment, barium nitrate was added to the solution to oppose the protecting action of gelatin and accelerate the coagulation of colloidal AgBr, and a lower concentration of gelatin was taken than in the actual case. Each solution for the dilute case was diluted with water up to 200 c.c. in which 10 g of barium nitrate was dissolved and this was titrated with the solution of 0.1 AgNO₃. The result is shown in Table 10.

Table 10.

Solutions titrated.				Results of titration mol %.	
0.1 KBr c.c.	0.1 KCl c.c.	2% gelatin c.c.	con. of gelatin.	with Ba.	with no Ba.
20.0	1.0	0.5	0.005 %	—	1.32
20.0	1.0	1.0	0.010 "	1.32	1.32
20.0	1.0	2.0	0.020 "	1.32	0.82
20.0	1.0	5.0	0.050 "	0.32	0.82
20.0	1.0	10.0	0.100 "	0.32	0.82

The results for the case of concentrated solutions are shown in Table 11. In this case, each solution was diluted with water only up to 40 c.c. and titrated with a solution of 1.0 AgNO₃ with no barium nitrate.

Table 11.

Solutions titrated.				Results of titration, mol %.	
1.0 KBr c.c.	0.1 KCl c.c.	mol ratio KCl : KBr	2% gelatin c.c.	with gelatin	with no gelatin.
20.0	1.0	0.005	0.5	0.00	0.00
20.0	2.0	0.010	0.5	0.00	0.09
20.0	5.0	0.025	0.5	0.00	0.13
20.0	10.0	0.050	0.5	0.13	0.44

From the difficulty of exact measurement of E.M.F., the results are not so regular as in other cases but are to be seen that gelatin hinders the precipitation of AgCl in AgBr. This seems to be due to the protecting action of gelatin which has a high gold number⁽¹⁷⁾ and for the reason described in (III) (E), this protection from rapid coagulation seems to reduce the precipitation of AgCl.

(b) Influence of ammonia.

The titration in the presence of ammonia is as difficult as in the above case. The instability of E.M.F. during the titration seems to come from the solution of AgBr in ammonia. Hence, an equivalent amount of dilute acetic acid was added to the solution just before the Br end and the remaining Br was titrated in the neutral state. The ammonia of 0.880 sp. gr. was added to the solution after it has been diluted with water to 20 times. The other conditions were exactly the same as in the preceding cases. The result in the case of dilute solutions is shown in Table 12 and that in the case of concentrated solutions in Table 13.

(17) Zsigmondy: *Kolloid Chemie.*, 4 Aufl. (1922) p. 173.

Table 12.

Solutions titrated.			Results of titration, mol %.			
1.0 KBr c.c.	0.1 KCl c.c.	NH ₃ c.c.	with no Ba.		with Ba.	
			no NH ₃	with NH ₃	no NH ₃	with NH ₃
20.0	1.0	2.0	2.50	1.08	0.34	0.00
20.0	2.0	2.0	4.17	1.67	0.50	0.17
20.0	5.0	2.0	8.38	2.17	0.67	0.34
20.0	10.0	2.0	10.34	4.27	0.84	0.34

Table 13.

Solutions titrated.			Results of titration.	
1.0 KBr c.c.	0.1 KCl c.c.	NH ₃ c.c.	with no NH ₃ mol %	with NH ₃ mol %
20.0	1.0	10.0	0.00	0.00
20.0	2.0	10.0	0.09	0.00
20.0	5.0	10.0	0.13	0.06
20.0	10.0	10.0	0.44	0.13

The remarkable difference in the titration with ammonia with no barium is that the precipitate coagulates strongly just as in the case with barium. And the results in both cases show that the presence of ammonia lowers the percentage of AgCl precipitation.

(c) Influence of potassium iodide.

The titration in the presence of a small amount of KI is much more difficult than in the case of ammonia. The precipitate in the case of dilute solutions with no barium remains as a transparent sol and the E.M.F. is extraordinarily unstable. The stability of the colloidal precipitate even at the Br end seems to come from the stabilizing action of AgI as condensation nuclei formed at the beginning of titration. The following result, shown in Table 14, was obtained by the addition of barium nitrate as in the other case.

Table 14.

Solutions titrated.				Results of titration mol % AgCl : AgBr
0.1 KBr c.c.	0.1 KCl c.c.	0.1 KI c.c.	mol Ratio KI : KBr	
20.0	0.5	0.0	0.00	0.43
20.0	0.5	2.3	0.01	0.59
20.0	0.5	5.0	0.25	1.09
20.0	0.5	10.0	0.05	1.25
20.0	0.5	20.0	0.10	1.25
20.0	0.5	50.0	0.25	1.50

According to this result, the higher the percentage of KI present, the greater is the amount of AgCl precipitation. The case of concentrated solutions and some other experimental conditions will be shown in the next section with other conditions together.

To sum up again, both gelatin and ammonia give a slightly lower percentage of AgCl precipitation while AgI, on the contrary, gives a slightly greater. These influences have certainly in part some close connection with the sensitivity of emulsions because the existence of sensitive nuclei in AgBr grains seems to be of primary importance for the high sensitivity of emulsions. But, the sensitivity of emulsions seems not to be directly connected only with the content of sensitive nuclei. There seem to be many other important factors which affect the sensitivity. Hence, the results above obtained must be seen to have only some relation to the sensitivity of emulsions.

(d) Precipitation of AgCl in the presence of gelatin, NH_3 and AgI.

In this experiment, the conditions at titration were taken as near as possible to those actually obtaining AgBr emulsions, within the limit of permitting the titration. Every solution to be titrated was diluted with water up to 50 c.c. and titrated with a solution of 1.0 AgNO_3 . The ammonia in the solution was neutralized just before the Br end by an equivalent amount of dilute acetic acid. The result is shown in Table

Table 15.

Solutions titrated.						Results of titration. mol % AgCl : AgBr
1.0 KBr c.c.	0.1 KCl c.c.	mol % KCl : KBr	10% gelatin c.c.	NH ₃ 0.880 c.c.	0.1 KI c.c.	
20.0	0.0	0.0	10.0	2.0	5.0	0.00
20.0	2.0	1.0	10.0	2.0	5.0	0.00
20.0	4.0	2.0	10.0	2.0	5.0	0.00
20.0	6.0	3.0	10.0	2.0	5.0	0.19
20.0	8.0	4.0	10.0	2.0	5.0	0.38
20.0	10.0	5.0	10.0	2.0	5.0	0.63

Of course the composition of each solution which was titrated was not exactly the same as in the actual case of the preparation of photographic emulsions. But, from the result of this experiment, it can be seen that the precipitation of AgCl together with AgBr in the photographic emulsion certainly occurs in some degree.

(V) CHEMICAL ANALYSIS OF AgBr EMULSION.

In the preceding sections, it was confirmed that some trace of AgCl must be contained in AgBr emulsions. In this experiment, 4 kinds of emulsions of commercial dry plates were examined electrometrically with regard to their halogen content to confirm if they really contain AgCl. The method of analysis first adopted in this experiment was that of Müller⁽¹⁷⁾. The silver halides in the emulsion of dry plates were extracted with a dilute KCN solution and this solution was titrated by the electrometric method with a solution of 0.1 AgNO₃. The result of this experiment was never constant though the greatest care was taken to keep the conditions as constant as possible. Such fluctuation in the results is considered, from the result of the blanc test, to come from the decomposition of KCN by absorption of CO₂ in air. The method of Clark⁽¹⁹⁾ was then tested and this method was proved by the blanc test to give an accurate result.

(18) Phot. Ind., 22 332 (1924).

(19) J. Chem. Soc., 749 (1926).

Therefore, this was adopted for this experiment, some points being a little modified.

(A) Soluble halides in AgBr emulsion.

Two quarter-plates were soaked over night in water in an ice cabinet, the plates being kept absolutely from active rays and the next morning were rinsed twice with fresh water, the plates being allowed to soak for 30 mins each time. The extracts obtained by the three washings were collected, and diluted with water up to 200 c.c. 10 g of barium nitrate was added and the whole was titrated with the 0.1 AgNO₃ solution. The result of the titration is shown in Table 16.

Table 16.

Samples of plates. (2 quarter plates)	Soluble halide expressed by 0.1 mol per litre.
Ilford extra rapid plates.	0.17 c.c.
Eastman 40.	0.08 "
Imperial Eclipse.	0.27 "
Cramer.	0.06 "

In this titration, it was impossible to determine the end points for Br and Br Cl separately so that it is not clear whether the amount obtained in Table 16 shows Br only or whether it denotes the sum of Br and Cl. In the next test, they were titrated after the addition of 2 c.c. of 0.01 KCl solution to each extract.

By such means, the end point only for Br could be found, which is shown in Table 17.

Table 17.

Samples of plates. (2 quarter plates)	Soluble halide expressed by 0.1 mol per litre.	
	Br'	Cl'
Ilford extra rapid plates.	0.155 c.c.	0.015 c.c.
Eastman 40.	0.060 "	0.020 "
Imperial Eclipse.	0.250 "	0.020 "
Cramer.	0.060 "	0.000 "

The amount of Cl was calculated from the difference between the result in Table 17 and that in Table 16. The greater part of soluble halides is found to be Br and the content of Cl, which may be looked upon as an impurity coming into the emulsion from any source, is very small.

In this case, it may be doubted whether the amount of halogens obtained above denotes really the whole of them or whether some part of the soluble halides is lost by adsorption by gelatin or by AgBr grains. But it was confirmed that not much is adsorbed by them. For this purpose, a mixture of AgBr emulsion and a certain amount of KBr was allowed to stand over night and the next morning, it was extracted with water in the same way as described above and the amount of Br was found by titration to be equal to that in the extract.

(B) Silver halides in AgBr emulsion.

Two quarter plates which were first washed in the same way as described above, were soaked in 100 c.c. of 0.1 KCN solution (Karlbaum's for analytical purposes) for 30 mins. and then were rinsed twice with 50 c.c. of fresh water, the plates being allowed to stand in it for 60 mins. each time. The extract and the washings were collected and poured into the flask A in Figure 4 with 10 g of pure granular zinc. It was boiled for an hour to eliminate silver from the solution in the form of metallic silver. Then 40 c.c. of 100% acetic acid diluted to 10 times with water, was added to the solution from funnel B and boiled for 2 hours to eliminate CN from the solution in gaseous form. During the boiling, air was sucked into the solution to accelerated the evolution of CN and to drive the excess of acetic acid from the solution. The solution thus prepared was filtered, diluted up to 240 c.c. and 12 g of barium nitrate was dissolved in it and then it was titrated as before with a solution of 0.1 AgNO₃. The result of titration is tabulated in Table 18.

Table 18.

Samples of plates. (2 quarter plates)	Silver halide expressed by volume of the solution 0.1 mol per litre.			mol % AgI : AgBr
	AgI	AgI AgBr	AgBr	
Ilford extra red plates.	0.45 c.c.	11.45 c.c.	11.00 c.c.	3.93
Eastman 40.	0.60 "	11.55 "	10.95 "	5.19
Imperial Eclips.	0.35 "	14.05 "	13.70 "	2.49
Cramer.	0.75 "	11.90 "	11.15 "	6.38

If the occlusion of KBr be neglected the amounts of halogens obtained in the result may be considered as the amount of the corresponding silver halides, as the soluble halides were completely eliminated from the plates. In some investigations, the content of silver is determined by another system of analytical method than for halogens and the difference between the result for the silver content and for the halogen content is taken as the amount of that existing in the free state. But it is very doubtful whether two different systems of analytical method could give the same degree of exactness and it may be possible for some error to be present from the difference in exactness, especially when the difference between the contents of the two is extraordinarily small.

The remarkable point in the above result is that all these plates seem to contain no AgCl and this result appears to contradict the present theory. But if we reflect in detail upon the nature both of the analytical method adopted for this experiment and of the method of preparation of AgBr emulsion, it may be considered that this is not necessarily the case.

In this analytical method, the amount of AgCl which precipitates together with AgBr is determined just at the moment at which the precipitation is finished so that the amount of AgCl shows the amount at this moment, but in the preparation of AgBr emulsion, the precipitate is digested in the presence of KBr and ammonia for a long time so that the greater part of AgCl which is contained in smaller grains is certainly converted at recrystallization into AgBr. The amount of AgCl which remains really in AgBr grains of emulsion after digestion, must be only that part which was

imbedded firmly in the larger AgBr grains and protected by AgBr particles against the action of solvent and KBr.

Thus, the content of AgCl in emulsion is reduced strongly by the digestion of the emulsion, so that it must be so extraordinarily small as to escape from the analytical result.

Accordingly, until a more sensitive analytical method is introduced, it may be difficult to obtain direct evidence for the existence of AgCl by analytical means. But from the many results obtained by titration described before, it may be easily deduced that a minute trace of AgCl exists in AgBr emulsions.

(VI) AgCl AS SENSITIVE NUCLEI.

From the results obtained by the numerous experiments described in the preceding sections, the existence of a minute trace of AgCl in the AgBr grains of photographic plates seems to be above suspicion and it is well known that in the case of visible change, the sensitivity of AgCl to light is greater than that of any of the silver halides and this was also experimentally shown in section (I). Hence, it may be easily to be imagined that such AgCl in AgBr grains will act as the sensitive nuclei both in visible darkening and in latent image formation in which AgCl will be first decomposed by light before AgBr begins to change and the metallic silver formed by the decomposition of AgCl will act as the development center at development. The following tests may be some evidences for the action of AgCl as sensitive nuclei:

(A) AgCl as sensitive specks in visible darkening of AgBr.

In this experiment, the silver bromide crystal was examined microscopically which was specially prepared in such condition so as to increase the content of AgCl in AgBr on the following way: At first, 10 c.c. of AgNO₃ solution (1.0 mol per litre) was added to the mixture of 11.0 c.c. of KBr solution (1.0 mol per litre) and 9.0 c.c. of KCl solution (1.0 mol per litre). The precipitate thus formed was washed and digested in dilute ammonia. By the microscopic examination of the crystal obtained above,

it was found that such AgBr crystal shows much more sensitive specks by the action of light than that prepared with no addition of KCl. The photo-micrograph ($\times 1100$) a in Figure 5 shows the former and b shows the ordinary one with no addition of KCl.

From this result, it may be considered that the sensitive specks which appear at the visible darkening of AgBr crystal are consisted of AgCl.

(B) Behaviour of AgCl in AgBr emulsion.

According to Eder⁽²⁰⁾, AgBr emulsions to which a little AgCl was added fog easily so that such emulsions can not be used for practical purposes.

Jacobsohn⁽²¹⁾ reports that AgBr plates treated with a dilute ammoniacal solution of AgCl shows much higher sensitivity than those not so treated and in "Photographische Industrie"⁽²²⁾, a method of preparing an emulsion is reported in which a little AgCl is precipitated together with AgBr. From these descriptions, it may be known that AgCl has certainly some effect on the sensitivity of AgBr. The present author also investigated the behaviour of AgCl in numerous kinds of AgBr emulsions but found that the addition of AgCl to the AgBr emulsion makes the tendency to fog greater even when the percentage of AgCl is very small. Of these results, the following shown in Table 19 is an example which illustrates the behaviour of AgCl comparatively well.

In Table 19, the iodo-bromide solution contained in one litre 0.98 mols of KBr, 0.02 mols of KI and 60 c.c. of ammonia (sp. gr. 0.880).

The AgNO₃ solution contains one mol of AgNO₃ per litre and full ammonia. After the precipitation of silver halides, 6 g of gelatin soaked in water was dissolved in each emulsion. The gelatin which was used throughout the investigations was that of Hasselt & Vilvorde, Bruxelles. The plates were prepared in the ordinary way after it was digested. The

(20) Eder's Handb., III (1903) p. 122.

(21) Brit. J. Phot., **76** 315 (1929).

(22) Phot. Ind., **27** 903 (1929).

exposure for sensitometry was 1.0 c.p. (international by half-watt lamp) 1.0 meter 1.0 min. The sensitivity was measured with Chapman Jones' plate tester (hereafter the same tester was used in every test).

The development by metol-hydroquinone at 15°C was continued until the plate began to fog. The result is shown in Table 19.

Table 19.

No.	Halides-gelatin solutions.				Ammoniacal 1.0 AgNO ₃	Time of digestion at 50 C.	Results	
	1.0 KBrI c.c.	0.1% gelatin c.c.	0.1 KCl c.c.	Water c.c.			Sensiti- vity.	Time of develop- ment.
1	25	1.0	0.0	24	24.75	5 mins.	14	6 mins.
2	25	1.0	0.0	24	24.75	30 "	18	6 "
3	25	1.0	5.0	19	25.25	5 "	18	3 "
4	25	1.0	5.0	19	25.25	30 "	22	3 "

Emulsions No. 3 and No. 4 to which 1.0 mol % AgCl was specially added, show much higher sensitivity than No. 1 and No. 2 respectively to which no AgCl was added but which were digested under the same conditions, and the former have a stronger tendency to fog than the latter. Thus, it is known that the addition of AgCl to AgBr emulsions gives higher sensitivity to the emulsion but fog more rapidly.

Accordingly, it may be said that the amount of AgCl necessary to form sensitive nuclei seems to be never large and that which precipitates from KCl contained in KBr as impurity may be sufficient.

(C) AgCl nuclei plates.

If the sensitive nuclei of AgBr grains are really AgCl, it may be said that the main function of photographic dry plates with regard to latent image formation depends on the AgCl contained therein and not on AgBr itself, and the AgBr may be considered to be only the material which supplies metallic silver to the development centres at development. If this is so, AgBr may be said not to be necessary in dry plates for their sensitiveness because metallic silver may be supplied to development centres by physical development after exposure to light, so that dry plates which

contain a minute trace of AgCl in the gelatin layer, in other words, AgCl nuclei plates, may be expected to perform the same function as ordinary AgBr gelatin plates. In this experiment, such AgCl nuclei plates were examined in the following way :

Solution B in Table 20 was mixed at 50°C from a burette with A which was agitated by a motor. The colloidal emulsion thus formed was digested at 50°C for 60 mins. and then the plates were prepared by the ordinary method. The sensitivity of AgCl nuclei plates was found to be unexpectedly low so that it was necessary for the plates to be exposed to day light for 60 mins. But it was found that the sensitivity of AgCl nuclei plates increased rapidly when other silver halides, especially a little AgI, were added. The results obtained in these experiments by physical development are shown in Table 20.

Table 20.

Halides solutions.			0.01 AgNO ₃ c.c.	Results.	
0.01 KCl	0.01 KBr	0.01 KI		Sensitivity	max. density
15 c.c.	—	—	13.5	4	0.13
—	15 c.c.	—	13.5	4	0.25
—	—	15 c.c.	13.5	4	0.06
10 "	5 "	—	13.5	5	0.08
10 "	—	5 "	13.5	12	2.12
—	10 "	5 "	13.5	3	0.13
7.5 "	7.5 "	—	13.5	8	0.21
7.5 "	—	7.5 "	13.5	13	1.61
—	7.5 "	7.5 "	13.5	4	0.03

From these results it is known that AgCl in the colloidal state never has high sensitivity for the formation of the latent image but that its sensitivity is increased when another silver halide, especially AgI, is added.

Thus the expectation failed in the result but in this result, it must be noticed that at least, the existence of AgCl is necessary for high sensitivity though it does not show high sensitivity unless some other silver halide is also present, because high sensitivity is shown only in emulsions

which contain AgCl.

From this fact, it may be at least said that the origin of the sensitiveness is AgCl itself but that its high sensitivity action is shown only with the aid of other silver halides.

(D) Emulsion containing two silver halides.

In the above section, it was found that nuclei plates prepared from AgCl emulsion containing another silver halide show higher sensitivity than those prepared from an emulsion consisting of pure AgCl. In this section, the object was to study the same matter more generally with ordinary emulsion. The emulsions used for this experiment are tabulated in Table 21. As is seen in the table, every emulsion contains a little of another silver halide varying from 0.0—4.0%. Excess of soluble halide at mixing in every emulsion was taken to the amount of 20%. At the precipitation of silver halides, the neutral AgNO₃ solution (1.0 mol per litre) was mixed from a burette with the alkali halides gelatin solution at 50°C.

Table 21.

mol %	1.0 AgNO ₃ added	AgI in AgCl	AgI in AgBr	AgCl in AgI
0.0	4.0 c.c.	(1) 1.0 KCl 5.0 c.c. 0.01 KI 0.0 "	(11) 1.0 KBr 5.0 c.c. 0.01 KI 0.0 "	(21) 1.0 KI 4.0 c.c. 0.1 KCl 10.0 "
0.5	4.02 "	(2) 1.0 KCl 5.0 " 0.01 KI 2.0 "	(12) 1.0 KBr 5.0 " 0.01 KI 2.0 "	(22) 1.0 KI 4.0 " 0.1 KCl 10.2 "
1.0	4.04 "	(3) 1.0 KCl 5.0 " 0.01 KI 4.0 "	(13) 1.0 KBr 5.0 " 0.01 KI 4.0 "	(23) 1.0 KI 4.0 " 0.1 KCl 10.4 "
2.0	4.08 "	(4) 1.0 KCl 5.0 " 0.01 KI 8.0 "	(14) 1.0 KBr 5.0 " 0.01 KI 8.0 "	(24) 1.0 KI 4.0 " 0.1 KCl 10.8 "
4.0	4.16 "	(5) 1.0 KCl 5.0 " 0.01 KI 16.0 "	(15) 1.0 KBr 5.0 " 0.01 KI 16.0 "	(25) 1.0 KI 4.0 " 0.1 KCl 11.6 "
mol %	1.0 AgNO ₃ added.	AgBr in AgCl	AgCl in AgBr	AgCl in AgI
0.0	4.0 c.c.	(6) 1.0 KCl 5.0 c.c. 0.01 KBr 0.0 "	(16) 1.0 KBr 4.0 c.c. 0.01 KCl 1.0 "	(26) 1.0 KI 4.0 c.c. 0.1 KCl 10.0 "
0.5	4.02 "	(7) 1.0 KCl 5.0 " 0.01 KBr 2.0 "	(17) 1.0 KBr 4.0 " 0.01 KCl 10.2 "	(27) 1.0 KI 4.0 " 0.1 KCl 10.2 "

mol %	1.0 AgNO ₃ added.	AgBr in AgCl	AgCl in AgBr	AgCl in AgI
1.0	4.04 c.c.	(8) 1.0 KCl 5.0 c.c. 0.01 KBr 4.0 "	(18) 1.0 KBr 4.0 c.c. 0.01 KCl 10.4 "	(28) 1.0 KI 4.0 " 0.1 KCl 10.4 "
2.0	4.08 "	(9) 1.0 KCl 5.0 " 0.0 KBr 8.0 "	(19) 1.0 KBr 4.0 " 0.01 KCl 10.8 "	(29) 0.1 KI 4.0 " 0.1 KCl 10.8 "
4.0	4.16 "	(10) 1.0 KCl 5.0 " 0.01 KBr 16.0 "	(20) 1.0 KBr 4.0 " 0.01 KCl 11.6 "	(30) 1.0 KI 4.0 " 0.1 KCl 11.6 "

50 c.c. of 10% gelatin was added to every mixture of alkali halides solution and then it was diluted with water up to 70 c.c.

By the preliminary test, it was found that these emulsions (except AgBr-AgI emulsion) give a fog from the beginning of development if they are warmed after washing. Therefore, each emulsion was coated directly after digestion without washing and the soluble part of the emulsion was removed from the emulsion by washing the coated plate. The exposure for sensitometry was 100 c.p. (for AgI plates 500 c.p.) 50 cms. 60 secs. After exposure the plates were developed with metol-hydroquinone developer at 15°C for 3 mins. The result is shown in Table 22.

Table 22.

mol %	AgI in AgCl					AgBr in AgCl				
	0.0	0.5	1.0	2.0	4.0	0.0	0.5	1.0	2.0	4.0
Digestion.	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
30' 50°C	4	11	13	15	15	4	5	5	5	6
60' "	5	14	17	22	×21	5	7	10	12	12
120' "	7	17	21	×22	×23	7	10	13	14	15
180' "	12	18	×18	×19	×23	12	11	14	16	17
mol %	AgI in AgBr					AgCl in AgBr				
	0.0	0.5	1.0	2.0	4.0	0.0	0.5	1.0	2.0	4.0
Digestion.	No. 11	No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18	No. 19	No. 20
30' 50°C	2	13	14	5	10	2	3	3	3	3
60' "	10	14	13	15	16	10	10	10	10	10
120' "	13	17	17	20	21	13	13	13	14	14
180' "	14	17	18	21	23	14	13	13	14	14

mol %	AgCl in AgI					AgBr in AgI				
	0.0	0.5	1.0	2.0	4.0	0.0	0.5	1.0	2.0	4.0
Digestion.	No. 21	No. 22	No. 23	No. 24	No. 25	No. 26	No. 27	No. 28	No. 29	No. 30
30' 50°C	0	0	0	0	16	0	0	5	8	13
60' "	0	9	10	10	18	0	0	5	8	13
120' "	0	10	11	10	18	0	0	5	8	13
180' "	0	10	12	14	20	0	0	5	8	13

Exposure 100 c.p. 0.5 meter 60 secs. for No. 1-20.

Exposure 500 c.p. 0.5 meter 60 mins. for No. 21-30.

Cross mark denotes fog.

Time of developments—3 mins. at 15°C.

According to this result, AgCl emulsion containing a little AgI generally shows the highest sensitivity, higher even than that of AgBr emulsion containing a little AgI. This shows just the same fact as in the above case of nuclei plates, and it is known that AgCl is of the first importance for high sensitivity but the presence of a little AgI in it is necessary for high sensitivity. The time of digestion for the AgCl emulsion containing a little AgI was limited on account of the fog formation. If the fog is not cared, the sensitivity of such emulsion might be increased by further digestion. On the other hand, the time of digestion for AgBr emulsion containing a little AgI was limited in order to keep the parallelism with other emulsions though it was found to be possible to increase the sensitivity much more by further digestion without giving any remarkable fog. The AgI emulsion containing a little AgCl shows fairly high sensitivity but its density is very small so that the sensitometric image is hardly visible.

(E) Visible darkening of the mixture of silver halides.

In this section, the visible darkening of the mixture of silver halides was studied in order to find the explanation for the change. The quantitative investigation of the visible darkening of single silver halides has been attempted by many workers. For example, Luther⁽²³⁾ tried it by potentio-

(23) Z. Phys. Chem., 30 628 (1899).

metric measurement, Schwarz and Gross⁽²⁴⁾ by determination of the halogen which separates from the halide and Weigert⁽²⁵⁾ by determination of metallic silver. But the results obtained by these authors seem not to have reached a final conclusion. Even in the case of a single silver halide, the matter stands in a such state. Hence, it goes without saying, that it is by no means an easy task to determine quantitatively the visible change of a mixture. The following test is only a comparison of the visible sensitivities of different mixtures containing any two of the silver halides, AgCl, AgBr or AgI. The combination of silver halides for this purpose is shown in Table 23.

Table 23.

mol %	AgI in AgCl		AgBr in AgCl		AgI in AgBr	
	o.1 KI	o.1 KCl	o.1 KBr	o.1 KCl	o.1 KI	o.1 KBr
0.0	(7) 0.0 c.c.	20.0 c.c.	—	—	0.0 c.c.	20.0 c.c.
0.5	(2) 0.1 "	19.9 "	0.1 c.c.	19.9 c.c.	0.1 "	19.9 "
1.0	(1) 0.2 "	19.8 "	0.2 "	19.8 "	0.2 "	19.8 "
2.5	(1) 0.5 "	19.5 "	0.5 "	19.5 "	0.5 "	19.5 "
5.0	(5) 1.0 "	19.0 "	(3) 1.0 "	19.0 "	1.0 "	19.0 "
10.0	2.0 "	18.0 "	(3) 2.0 "	18.0 "	2.0 "	18.0 "
25.0	5.0 "	15.0 "	(4) 5.0 "	15.0 "	5.0 "	15.0 "
50.0	10.0 "	10.0 "	(6) 10.0 "	10.0 "	10.0 "	10.0 "

mol %	AgCl in AgBr		AgBr in AgI		AgCl in AgI	
	o.1 KCl	o.1 KBr	o.1 KBr	o.1 KI	o.1 KCl	o.1 KI
0.0	—	—	0.0 c.c.	20.0 c.c.	—	—
0.5	0.1 c.c.	19.9 c.c.	0.1 "	19.9 "	0.1 c.c.	19.9 c.c.
1.0	0.2 "	19.8 "	0.2 "	19.8 "	0.2 "	19.8 "
2.5	0.5 "	19.5 "	0.5 "	19.5 "	0.5 "	19.5 "
5.0	1.0 "	19.0 "	1.0 "	19.0 "	1.0 "	19.0 "
10.0	2.0 "	18.0 "	2.0 "	18.0 "	2.0 "	18.0 "
25.0	5.0 "	15.0 "	5.0 "	15.0 "	5.5 "	15.0 "
50.0	10.0 "	10.0 "	10.0 "	10.0 "	10.0 "	10.0 "

(24) Z. anorg. Chem., 133 389 (1924).

(25) Z. Phys. Chem., 99 499 (1921).

To each solution of potassium halides shown in Table 23, 20 c.c. of 0.1 AgNO_3 solution was added. These mixtures of silver halides were exposed to daylight all at once in paraffin cavities after washing and elimination of the greater part of water. The visible sensitivity of these mixtures depends in some degree on the compactness and the percentage of moisture. But on the whole, the numbers in brackets in Table 23 give the order of those which have the highest sensitivity.

This result coincides exactly with that obtained in the above section for latent image formation. Thus the sensitivity both for latent image formation and for visible darkening seems to be analogous in the case in which the sensitive materials were prepared under the same conditions with regard to composition.

Secondly, the visible darkening of the combination of two silver halides in contact instead of mixed was studied. Each silver halide was precipitated from its respective solution (0.1 mol per litre) an equivalent amount of AgNO_3 being mixed with each. The precipitate was washed, pressed between filter papers to remove the moisture and dried. A small piece of a silver halide was pressed into another in the combinations given in Table 24.

Table 24.

No.	1	2	3	4	5	6
A small prece of	AgBr	AgI	AgI	AgCl	AgCl	AgBr
was introduced into	AgCl	AgCl	AgBr	AgBr	AgI	AgI

On being exposed for several hours for direct daylight, the environs of the small piece in the first three pairs darkened more intensely than the other parts just like a halation in photographic negatives. This phenomenon was most marked in the second pair. On the contrary, in the last three pairs, the small piece which is pressed into another silver halide darkened more intensely than that which was exposed in single state and its degree was most remarkable in the fifth pair.

The relation between the halides both in the first three pairs and in

the last three pairs is quite the same and these results coincide again with those obtained in the above two cases. These relations may be expressed generally as follows:

When two silver halides are exposed in contact to light, the darkening of the silver halide having smaller molecular weight is accelerated by the influence of the other having a larger molecular weight and this influence is most marked when the difference between their molecular weights is greatest. Wherein does this change consist? The two halides were precipitated separately and they were brought into contact after drying. Therefore, the formation of a double compound or a solid solution can not be expected. It seems as if there is no intercourse between the two, but here it must be noted that every one of the two evolves respective halogen gas on exposure to light and the halogen gas thus evolved from the one will certainly diffuse into the other. In this case, it is well known that a halogen gas having a smaller atomic weight converts a silver halide which combines with a halogen having a greater atomic weight, into its own halide, and this is used in gravimetric determination of halogens from their mixture⁽²⁶⁾.

For example, chlorine gas converts AgBr or AgI into AgCl and bromine gas converts AgI into AgBr and this relation is quite reversed in the case of halogen ions in solutions with silver halides. Not only this relation, but also the following remarkable phenomenon occurring between halogen gas and silver halide was observed: One of the silver halides was introduced into a closed bottle containing iodine, liquid bromine or chlorine water in the combinations given in Table 25.

Table 25.

No.	1	2	3	4	5	6
A little precipitate of	AgI	AgBr	AgCl	AgI	AgBr	AgCl
was introduced into the bottle containing	chlorine water	iodine	iodine	bromine water	chlorine water	bromine water

(26) Fresenius: Chem. Analyse., 6 Aufl. (1903) p. 662.

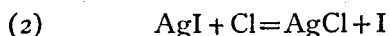
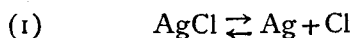
In pairs No. 1, No. 2 and No. 3, the silver halide darkens rapidly owing to the action of halogen vapour when it is introduced into the vessel, the intensity being in the order of their numbers in the Table.

If these darkened silver halides are washed with water, they are bleached to their own color. Therefore, this darkening may not be a chemical change but rather seems to be the result of the condensation of halogen vapour upon the halides. In pair No. 4, the condensation of bromine vapour upon AgI is most marked but the darkening does not take place in this case. In the pairs No. 5 and No. 6, no marked change is observed.

The condensation of halogen vapour on silver halides occurs in the dark exactly in the same manner as in light. Therefore, this phenomenon may not be considered to be due to light. If these facts are applied to the visible darkening of a mixture of silver halides, the acceleration of visible darkening may be explained as follows :

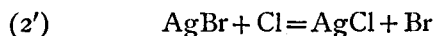
At first, it must be borne in mind that the photo-decomposition of silver halides is reversible so that the concentration of the decomposition product affects the change. For example, it is well known that various halogen accepters accelerate the photo-decomposition of silver halides. Now, if two silver halides such as AgCl and AgI in contact are exposed to light, the chlorine and the iodine vapour produced by the decomposition, will condense respectively on the other silver halide. In this way, the decomposition of AgCl seems to be much accelerated by the presence of AgI.

In other words, AgI acts as a chlorine acceptor and from the result above described, AgI seems to be the strongest chlorine acceptor. From these results of observation, it may be said that if an AgCl nucleus comes into contact with AgI within an AgBr grain, its sensitivity will become much higher. The chlorine vapour thus absorbed by AgI will react with it. These chemical changes may be denoted as follows :



The new AgCl which was formed by the secondary reaction will

be decomposed by further action of light and so on. If AgCl comes into contact with AgBr, the same kind of reaction as the above will take place as follows :



Thus the photo-decomposition of AgCl sensitive nuclei which are in contact with other silver halides within the AgBr grain seems to occur by chain reactions. The failure of intermittency may depend partly on the secondary reaction above described which occurs even in the dark interval between the exposures and makes the AgCl sensitive nuclei a little larger without the aid of light.

(E) Nature of latent image formation.

It is not yet conclusively determined whether the mechanism of the latent image formation is really the same or quite different one as that of the visible darkening. But, from the results of observations above described, it may be deduced that the former in its nature is not different from the latter. In other words, the change in the case of latent image formation is probably the earliest stage of that in the case of visible darkening of AgCl. The high sensitivity of the former depends on one side on the sensitizing action of AgI, AgBr or gelatin and on the other side, it depends on the fact that the former occurs only in the highest part of velocity in the reversible reaction.

(VII) FORMATION OF AN EMULSION AND THE AgCl NUCLEI.

In this section, an attempt was made to explain the formation of AgBr gelatin emulsions mainly from the standpoint of AgCl nuclei.

(A) Action of gelatin in emulsions.

Hitherto, the nature of the sensitive nuclei has been treated without any reference to the existence of gelatin in them. But it is a well-known fact that gelatin plays an important rôle in the emulsion, so that the theories of sensitive nuclei that have appeared up to now attribute their origin to gelatin. In the present investigation, it was stated in section (I)

that the sensitive nuclei of AgBr appear even in the absence of gelatin. Accordingly, here the action of gelatin will be treated only with regard to the other part of its function in emulsions. Now the action of gelatin may be divided into parts as follows :

(a) Gelatin as a protecting colloid in emulsion.

That gelatin has a strong protective action against the coagulation of colloidal particles is a well-known fact and this certainly takes place in the case of photographic emulsions. If AgBr is precipitated in the presence of gelatin, the coagulation of the primary particles of AgBr is much interrupted by the gelatin. Consequently, the individual grains of AgBr in an emulsion are isolated from each other by a layer of gelatin. On the other hand, AgBr forms a coagulum if it is precipitated from an aqueous solution of such a high concentration as is used in the case of the precipitation of AgBr in photographic emulsions. This difference has an important effect on the reducibility of AgBr by a developer.

If AgBr precipitated from an aqueous solution is developed in red light, it is reduced in a few minutes completely to metallic silver, but that precipitated from a gelatin solution is reduced in a very long time, say after one hour's development.

The cause of this difference occurring at development is explained by many theories. According to Mess and Sheppard⁽²⁷⁾, the gelatin acts as a filter against nuclei. This is meant only for the case of development of an exposed plate, and the nuclei in the AgBr precipitated in a gelatin solution and not exposed to light must be different from those mentioned in this theory. The present author believes such nuclei to be formed at the precipitation of AgBr in the absence of gelatin from AgBr itself; this will be explained later in the section on the nature of fog.

Thus, one of the functions of gelatin in the preparation of an emulsion seems rather to be the prevention of the formation of fog. It is not necessary to explain here the function of gelatin at development, as it has been clearly explained by Mees and Sheppard. Thus, the function of

(27) Investigations on the theories of photographic process., (1907) p. 207.

gelatin as a protecting colloid may be said to be twofold that in the preparation of emulsions and that at development.

(b) As a halogen acceptor.

In the above section, the action of gelatin at the precipitation of AgBr and at the development of plates was discussed. In this section, the action of gelatin at the exposure of plates to light i.e., the action of gelatin for the sensitivity of plates was studied.

Cross and Bevan⁽²⁸⁾ state that, when chlorine acts with protein, the amino group of it becomes chloramine and Siegfried and Peppin⁽²⁹⁾ showed that the absorption of halogen varies according to the degree of hydriasis of gelatin and the larger such is, the smaller is the halogen absorption. In the present study, the absorption of chlorine by various commercial gelatin for photographic purpose and a kind of commercial agar-agar was examined. To determine at first the chlorine content in gelatin, 2.0 g of each sample and 10.0 g of barium nitrate were dissolved in 200 c.c. of water and the amount of chlorine was determined by electrometric titration with the solution of 0.01 AgNO₃. Another 2.0 g of each sample was soaked for 15 hours in 200 c.c. of a dilute solution of chlorine (30 times dilution of saturated chlorine water) and another 2.0 g of each was soaked for two hours in 100 c.c. of saturated chlorine water. All of them were washed completely and the amount of chlorine in the gelatin was determined by the same method as above. The results of titration are shown in Table 26.

Table 26.

Samples of gelatin.	Cl' content expressed by 0.01 AgNO ₃	Cl' absorbed from dil Cl' water. expressed by 0.01 AgNO ₃	Cl' absorbed from conc. Cl' water. expressed by 0.1 AgNO ₃	Cl' absorbed from conc. Cl' water. %
Hasselt-Vilvorde	0.5 c.c.	0.70 c.c.	8.55 c.c.	1.47 %
Winterthur hard.	0.0 "	0.90 "	8.55 "	1.47 "
Winterthur soft.	—	—	10.25 "	1.81 "
Deutsche (8638)	0.14 "	0.30 "	10.35 "	1.81 "
Nelson (6272)	0.14 "	0.20 "	9.35 "	1.66 "
Stoess (4020)	0.20 "	0.30 "	10.05 "	1.78 "
Kreuz (5027)	0.20 "	0.10 "	10.85 "	1.92 "
Koepff (99)	0.10 "	0.20 "	—	—
Agar-agar	0.12 "	0.12 "	0.00 "	0.00 "

(28) J. S. C. I., **27** 1187 (1908).

(29) Chem. Abst., **9** 2905 (1915).

Of course these amounts of chlorine absorption were examined only relatively because gelatin dissolves no more at its full absorption. At any rate, it is known from these results that each sample of gelatin absorbs fairly large amount of chlorine, not varying much according to the sample, and that agar-agar shows no absorption of chlorine.

Then the preparation of agar-agar AgBr plates was investigated with over 100 emulsions but it was found that the sensitivity of these plates was only about 1/500 of that of the high speed commercial plates. The method which was found to be best for the preparation of agar-agar plates was as follows :

A solution.	agar-agar (2%)	900 c.c.
	NH ₄ Br	12 g.
	KI (10%)	2 c.c.
B solution.	AgNO ₃	10 g.
	water	30 c.c.
	ammonia	full

The B solution at 20°C is mixed with A solution at 70°C. Then it is digested for three hours at 70°C. The emulsion thus prepared is coated directly on glass plates and then it is washed and dried. The characteristics of the agar-agar plates are their easy acceptance of the action of color sensitizer by which not only the color sensibility but also the general sensibility is increased to the level of high speed commercial plates and the high sensibility to the ultra-violet ray owing to the transparency of agar-agar to the same ray. The details will be reported at the next opportunity.

At any rate, the higher sensitivity of gelatin plates compared with that of agar-agar plates may be attributed partly to the action of gelatin which absorbs halogen much more than agar-agar.

The fundamental action of gelatin as the chlorine acceptor for AgCl may be observed in the following manner :

If AgCl precipitate is exposed to light after the addition of a minute drop of dilute gelatin solution on its surface, the visible darkening at the

position of the gelatin drop is much stronger than at the other part where there is no gelatin. The visible darkening of a colloidal suspension of AgCl, which is comparatively stable towards the light action on account of its adsorbed ion, is much accelerated by the addition of a small amount of gelatin solution.

Now, it is well known that emulsions prepared under exactly the same conditions with different samples of gelatin vary in some case in sensitivity. Many explanations have been given for such variation in sensitivity caused by different samples of gelatin. The latest and representative explanation of them is the silver sulphide theory of Sheppard's⁽⁴⁾, in which the content of some sulphur compound in the gelatin is considered to be the direct cause of such variation in sensitivity. But in the present paper, it was stated in section (I) that there is another origin of sensitive nuclei. Therefore, the following emulsion was examined to find out whether such variation in sensitivity comes from difference in the absorption of halogen by different samples of gelatin. The emulsions for this purpose were prepared by mixing 10.0 c.c. of 1.0 AgNO₃ (ammoniacal) with a mixture of 10.5 c.c. of 1.0 KBr, 3.0 c.c. of 0.1 KI and 50 c.c. of 10% solution of gelatin at 50°C, varying only in the sample of gelatin.

The digestion before washing of the emulsions was 60 mins. at 50°C and those after washing were 60 mins. at 50°C and 120 mins. at 50°C. The sensitivity of each emulsion is tabulated in Table 27. The exposure for sensitometry was 1.0 c.p. 1.0 meter 15 secs.

Table 27.

Samples of gelatin.	2nd. digestion 60'50°C	2nd. digestion 120'50°C
Hasselt-Vilvorde.	16 clear	17 clear
Winterthur hard.	12 "	13 "
Winterthur soft.	11 "	12 "
Deutsche (8638)	11 "	12 "
Nelson (6270)	18 Fog density 0.51	18 Fog density 1.10
Stoess (4020)	14 Fog density 0.21	15 Fog density 0.43
Kreuz (5027)	19 Fog density 0.18	20 Fog density 0.40
Koepff (99)	18 clear	19 clear

According to this result, there can be found no parallelism between the halogen absorption of gelatin and the sensitivity of the plate which was prepared with the same sample of gelatin. Hence, the factor which affects the sensitivity of the plate according to the sample of gelatin must be something other than the halogen absorption of gelatin and this unknown factor seems to be related to a more important feature of the digestion of an emulsion which affects the sensitivity of the emulsion. The following result of a study of the protective power of each sample of gelatin gives some idea as to the variation in sensitivity according to the sample of gelatin. In this experiment, 20 c.c. of 0.1 AgNO₃ solution was added to a mixture of 25 c.c. of 0.1 KBr, 5 c.c. of 5% gelatin and 270 c.c. of water. The density of AgBr suspension thus prepared was measured by the thermopile nephelometer. The result of the measurements is shown in Table 28.

Table 28.

Samples of gelatin.	Sensitivity of plate prepared with respective gelatin from table 27.	Density/cm. of suspension.	
		after one day.	after 2 days.
Kreuz (5027)	20	0.114	0.237
Koepff (99)	19	0.097	0.194
Nelson (6270)	18	0.092	0.180
Hasselt-Vilvorde	17	0.092	0.180
stoess (4020)	15	0.081	0.137
Winterthur hard	13	0.076	0.125
Deutsche (8638)	12	0.076	0.120
Winterthur soft	12	0.076	0.120

From this result, it is known that the order of the protecting power of each sample of gelatin has some connection with that of the sensitivity of the plates which were prepared with the respective sample of gelatin. It will be explained in the following section how important the coagulation of AgBr in photographic emulsion is with regard to the sensitiveness of plates.

Thus, the variation of sensitivity according to the samples of gelatin seems to depend on the physical consistency of the gelatin rather than on

its chemical properties. Here it must be noted that in this experiment the sensitivity was compared with reference to emulsions prepared under the same conditions. Hence, the result does not show the absolute value of gelatin for photographic purpose. The properties of plates may vary with the conditions of preparation even with the same sample of gelatin or the same result may be obtained with different samples of gelatin by regulation of the method of preparation.

(B) Ripening of emulsion.

There are many theories of ripening proposed by many authors from the standpoint of various features of emulsion. But on the whole, these theories all start from the premise that the sensitive material in photographic plates is assumed to be AgBr. The only exception is the colloid silver theory proposed by Renwick⁽³⁰⁾ in which the sensitive material is taken to be colloid silver. Therefore, the sensitiveness of silver halides in dry plates is not taken into consideration in this theory. But it is a little doubtful whether it is correct to neglect the sensitiveness of silver halide altogether. In the present paper, it is intended to explain the ripening of emulsion by AgCl sensitive nuclei.

Consequently, the mode of explanation is bound to be a little different from others.

(a) Precipitation of silver halide in gelatin solution.

In preceding sections, only the occlusion of a minute trace of AgCl was considered at the precipitation of AgBr. But in the case of precipitation of AgBr in a gelatin solution, it must be noted that some trace of gelatin may be occluded in the precipitate or in the crystal lattice of AgBr by exactly the same mechanism as in the occlusion of AgCl which is described above. It is believed by many authors that there is an admixture of gelatin in AgBr grains. For example, according to Ostwald⁽³⁰⁾, gelatin forms a new compound with AgBr in the emulsion, and Bancroft⁽³¹⁾ is of

(30) Eder's Jahrb., (1905) p. 3.

(31) J. Phys. Chem., 14 620 (1910).

opinion that gelatin forms a complex with AgBr and water. Thus, these authors attribute the existence of gelatin in AgBr grains to a chemical combination. The basis for these theories is derived from the high sensitivity of dry plates, which these theories hold to be due to the existence of gelatin with AgBr. But in the present investigation, such a reason for supposing this combination to be a chemical one is not found to be necessary because the sensitiveness of dry plates is believed to be due to the AgCl sensitive nuclei.

The combination of two substances which are apparently not reactive, is explained in some cases by adsorption or by the formation of a solid solution, from the relation between the amount of adsorption and the concentration of the second substance or from the deformation of the crystal lattice. The admixture of gelatin in AgBr may be explained in such a manner but in the present paper, it will be explained simply by occlusion at precipitation because the rapid coagulation of primary particles at precipitation may occur within the limit of the thickness of the gelatin layer in which the coagulation of primary particles is not at all disturbed.

Thus, the AgBr grains precipitated in a gelatin solution are considered, in the present paper, as a mechanical mixture in which pure AgBr particles and a little pure AgCl particles are dispersed in the gelatin medium. The state in which these substances are mixed at precipitation may be considered as follows :

At the precipitation of AgBr, AgNO₃ solution is rapidly added to the mixture of KBr and gelatin solution, and then the density of the insoluble AgBr particles increases rapidly in the gelatin solution.

The particles thus formed coagulate rapidly owing to the influence of the electrolyte opposing to the protecting action of gelatin. But a minute trace of gelatin will be occluded in the free space between the primary particles within the coagulum. Thus, in the secondary aggregate formed by rapid coagulation or by the rapid recrystallization, many colonies of pure silver halide will exist, each of them being isolated by a thin layer of gelatin. In exactly the same manner, tertiary aggregates may be formed and so forth. This state of aggregation within the AgBr grain may be considered

to be analogous to that of the whole emulsion in which AgBr grains are finely dispersed in gelatin. Thus, in the photographic emulsion, primary, secondary etc. dispersed systems may be imagined.

(b) Colloidal emulsion.

In the preceding sections, it was explained that the occlusion of AgCl nuclei within the AgBr grain is a phenomenon which occurs at a rapid coagulation of the precipitates. Hence, it is obvious that the colloidal emulsion does not contain not so many AgCl nuclei as ordinary emulsions because the degree of coagulation in colloidal emulsions is much less than that of ordinary ones. Even when AgCl nuclei exist in colloidal grain of AgBr, they will be isolated by a gelatin layer, as explained above, so that their sensitivity is much lower than in the case where they are in direct contact with other silver halides, and moreover they cannot act as development centres because the metallic silver reduced out by the action of light from AgCl is isolated from the main body of AgBr at development.

Hence, for the colloidal emulsion, the exposure must be so long that as AgBr itself is decomposed partly to Ag and Br by light. In fact, it is well known that a colloidal emulsion has an extraordinarily low sensitivity so that no experimental evidence is required, some times its sensitivity being only one ten-thousandth of that of rapid plates.

(c) Conditions of precipitation of AgBr and its ripening.

That the condition in which the emulsion is precipitated has a great influence on the ripening of emulsion is a well known fact. For example, Lüppo Cramer³²⁾ has shown that the sensitivity of an emulsion which was precipitated in the colloidal state will not be much higher though it is digested afterwards, but the initial stage of emulsion making is of much greater importance than the later steps of the process.

Thus, it is obvious that the condition of an emulsion at the precipitation predominates in the ripening of the emulsion. The explanation of this may be derived from the foregoing conception of precipitation as follows :

(32) Photo. Probleme., (1907) p. 35.

If an emulsion is precipitated in a high concentration of precipitants, in low concentration of gelatin, at high temperature or in the presence of solvents of AgBr (KBr or ammonia), the precipitate of AgBr will coagulate rapidly or recrystallize rapidly so that AgCl nuclei will come directly in contact with AgBr or AgI within the AgBr grain or at least, the thickness of the gelatin layer which isolates the AgCl nuclei may be much less than that in the case of colloidal emulsions so that the distance between the AgCl nuclei and AgBr or AgI within the AgBr grain will be less. This condition of the AgBr grain renders the ripening more easier at digestion, as is explained in the next section.

(d) Ripening of emulsion by digestion.

It is well known that the sensitivity of an emulsion is increased by the digestion at a suitable temperature for a suitable time. What kind of change affects the sensitivity of an emulsion in this stage?

Up to the last section, the foreign substances which are occluded in AgBr grains at precipitation were limited only to AgCl and gelatin. But here it must be noted that all the substances which exist in the phase of AgBr precipitation must be considered to be occluded within the grain in some minute amount for the same reason as before that is, a minute trace of ammonia, water, KBr or KNO_3 will be occluded.

Now, if the AgBr grain which contains such numerous substance is digested, a slow recrystallization of AgBr and AgCl particles will occur within the grain. An amount of AgCl equivalent to that of the KBr which is occluded within the grain will be converted into AgBr when the solution of AgCl comes into contact with that of KBr. The remaining AgCl will be diffused in the form of a solution through the gelatin layer within the grain and it will be deposited again on the surface of AgBr or AgI particles.

Thus, the AgCl nuclei come into contact with other silver halides by slow recrystallization which occurs within the grain at digestion. The sensitivity of the grain in which AgCl nuclei come into direct contact with AgBr or AgI as above, will be much higher for the reason described in the foregoing section. The time taken for the diffusion of AgCl solution

through the gelatin layer will depend on the thickness of the gelatin layer which isolates the AgCl nuclei from other silver halides. Hence, it follows that the condition in which AgBr precipitates, is the predominating influence in the ripening of emulsions.

Such slow recrystallization within the grain is accompanied by that of AgBr grains themselves, which affects the size of the grains in an emulsion. This will be treated later under the heading of the grain size of emulsions.

Secondly, the change which occurs in the course of recrystallization at digestion is the conversion of AgCl nuclei into AgBr by the action of KBr. At this stage, the comparatively smaller AgBr grains will be dissolved by solvents (KBr solution or ammonia) and the AgCl particles which were occluded in these smaller AgBr grains will be converted into AgBr before being deposited again on the surface of larger grains. Thus in the course of digestion, the ripening and the loss of AgCl nuclei occur at the same time, their degree being dependent on the conditions under which the emulsion is digested.

The AgCl sensitive nuclei occluded in larger AgBr grains which do not dissolve at recrystallization, will not be much attacked by KBr, and they will only ripen during the digestion.

Lastly, the standing of an emulsion after first digestion at a lower temperature may be considered as a special digestion in which the temperature of digestion is specially lowered and the velocity of recrystallization is very small. The effect of such digestion will depend on the original nature of the emulsion and the conditions under which the emulsion is allowed to stand. The second digestion of a washed emulsion is also a special one in which the emulsion does not contain any solvent of silver halides except water. The important characteristic of this digestion is the absence of Br⁻ which converts the AgCl nuclei to AgBr and the absence of ammonia which increases fog and grain size. Consequently, this digestion may be considered to be the most favorable one in which mainly the ripening of the emulsion occurs, but not the loss of sensitive nuclei, not much occurrence of digestion fog and not much increase in grain size.

(C) **Origin of fog.**

The formation of fog is closely connected with the sensitiveness and the developability of silver bromide grains. What are known generally as the causes for the formation of fog at the preparation of emulsions are the digestion of emulsion in comparatively dilute solution of KBr or gelatin, the digestion in comparatively concentrated ammonia and over-digestion at any condition. The origin of fog which appears by these treatments is probably not only one but there may be various ones. That the fog is eliminated or reduced by the addition of a little KBr to the washed emulsion is also a noticeable fact which is related to the nature of the origin of fog.

From these facts, the origin of fog seems to be related to the action of KBr and ammonia on AgBr grains. The normal AgBr grain which does not fog easily may be considered to contain some moderate amount of KBr in the form of occlusion or adsorption and that which fogs rapidly by developer to contain no or little KBr. The AgBr grain deposited rapidly from ammoniacal solution contains probably little KBr but the presence of much KBr in emulsion at the recrystallization by ammonia seems to increase the amount of KBr in AgBr grains.

The AgCl nuclei which are contained in AgBr grains may be considered to be an origin of fog which will be described later in the heading of Developability of AgBr grains.

As it is explained by many authors, another probable origin of fog is the metallic silver produced by the reduction of silver bromide by the decomposition product of gelatin. This may be true if silver bromide is really reduced to metallic silver at digestion because the emulsion to which a little Bredig's colloidal silver was added and then digested fogs strongly both at chemical and at physical development.

By the analogous reason, the impurity contained in commercial silver nitrate may be considered to be an origin of fog.

If the dilute solution of commercial AgNO_3 is examined by a slit ultramicroscope, it will be found that it contains with no exception some

insoluble colloidal matter which does not disappear on the addition of nitric acid and the number of particles increase on exposure to sunlight. If a drop of dilute KCl solution is added to AgNO_3 solution from which such colloidal particles have been eliminated by ultrafiltration, it will be found that the particles which have exactly the same behaviour as the above increase in number. From these facts, such impurity in AgNO_3 seems to be some minute trace of AgCl derived from the soluble chloride contained in the materials of AgNO_3 or from the apparatus used for its manufacture or its transportation.

Such AgCl contained in AgNO_3 will be certainly decomposed during various treatments by light giving a trace of photochloride which will be again decomposed to metallic silver by ammonia in ammoniacal AgNO_3 solution. If such silver particles be introduced into the AgBr grain, they will induce the reduction of AgBr at development, i.e., they will be an origin of fog. On the other hand, it was found that an emulsion prepared with AgNO_3 which was crystallized from a solution obtained by dissolving pure silver in Cl-free nitric acid in the dark room, showed as much fog as that prepared with commercial AgNO_3 .

Therefore, it is clear that such silver contained in AgNO_3 is not the only source of fog.

(D) Action of AgI.

It is an interesting phenomenon that the addition of AgI in a small percentage to the AgBr emulsion increases the sensitivity of the emulsion though AgI itself has much lower sensitivity both in the form of an emulsion and in visible darkening than AgBr. Various explanations have been given for this problem but owing to the lack of any explanation of the sensitiveness of AgBr emulsions, they seem to be still not conclusive.

However that may be, the primary change which occurs apparently in AgBr emulsion on the introduction of a small amount of KI at the beginning of precipitation seems to be the formation of condensation nuclei consisting of colloidal AgI for the precipitation of AgBr, and the precipitate of AgBr will be dispersed in much finer suspension.

Of course, the action of AgI in this case depends on the form of AgI which precipitates first.

The precipitate of AgBr will be finely dispersed only when AgI is precipitated in the colloidal state. The results, which vary according to the mode of introduction of KI into emulsions, have been often a matter of argument. But it may be considered that the primary cause of such variation in results depends mainly on the action of AgI as condensation nuclei at the precipitation of AgBr. The following result of measurements shows how AgI makes the AgBr emulsion finer at its precipitation. In this experiment, the number of AgBr grains in emulsions which were prepared in the ordinary way with varying percentages of AgI was counted by means of Thoma's Haemocytometer on a microscope illuminated by a mirror condenser. The result is shown in Table 29.

Table 29.

AgI % in AgBr	Number of grains				Number of grains in emulsion from 1 g AgNO ₃
	1st. counting	2nd. counting	3rd. counting	mean	
0.0	1002	1076	1206	1094	180×10^{10}
1.0	1788	1680	1926	1798	295×10^{10}
2.0	1932	2124	2456	2170	360×10^{10}
4.0	1936	2142	2728	2268	372×10^{10}
8.0	2492	1448	—	2470	495×10^{10}
10.0	2680	2688	2512	2926	430×10^{10}

From this result, it is clear that the effective percentage of AgI in AgBr from the point of view of making emulsions finer is in the neighbourhood of 2%, which coincides on the whole with that in most cases of commercial emulsions. Now, it is a well-established fact that there exists no exact parallelism between the size of a grain and its sensitivity. Then it follows from the foregoing that some other change which happens in the AgBr grain going parallel to the diminishing of grain size may affect the sensitivity. Such unknown change caused by AgI may be considered to be the introduction of a trace of AgI into every grain of AgBr, because the nucleation of AgI is the predominating influence in the

diminution of the size.

The action of AgI on AgCl nuclei at exposure was explained in the preceding section. Hence, the function of AgI may be said to be the sensitizing action on the AgCl sensitive nuclei coming into every AgBr grain as condensation nuclei at precipitation, and the diminishing of the grain size by AgI may be said to accompany this only by chance without having any direct effect on the sensitivity. The effective percentage of AgI in AgBr depends probably on the necessary amount of AgI as nucleus for every AgBr grain at precipitation and if it is excessive for the nuclei, the excessive part will not show any favorable effect for the sensitizing of AgCl nuclei.

(E) Experiments showing some features of the formation of emulsions.

The known factors which have some influence on the sensitivity of emulsions are so many that the examples of even a few thousand emulsions hardly cover all the possible cases. In this experiment, some features of the formation of emulsions are shown only by a few examples which include the influence of the molar percentage of AgI, the concentration of ammonia, the concentration of KBr, the time of digestion both before (1 st.) and after (2 nd.) the washing of the emulsion and the time the emulsion is allowed to stand before washing. The emulsions used for this experiment are tabulated in Table 30.

Table 30.

1.0 AgNO ₃ used.		AgI mol %	0.0		3.0		6.0	
Ammoniacal.	Neutral.		dil.	conc.	dil.	conc.	dil.	conc.
2 c.c.	8 c.c.	1.0 KBr	10.5 c.c.	15.0 c.c.	10.5 c.c.	15.0 c.c.	10.5 c.c.	15.0 c.c.
		0.1 KI	0.0 "	0.0 "	3.0 "	3.0 "	6.0 "	6.0 "
		10% gelatin	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "
		Water	10.5 "	9.0 "	4.5 "	3.0 "	4.5 "	0.0 "
5 c.c.	5 c.c.	1.0 KBr	10.5 "	15.0 "	10.5 "	15.0 "	10.5 "	15.0 "
		0.1 KI 0.1	0.0 "	0.0 "	3.0 "	3.0 "	6.0 "	6.0 "
		10% gelatin	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "
		Water	10.5 "	6.0 "	4.5 "	3.0 "	4.5 "	0.0 "

1.0 AgNO ₃ used.		AgI mol %	0.0		3.0		6.0	
Ammoniacal.	Neutral.	Concent of KBr	dil.	conc.	dil.	conc.	dil.	conc.
10 c.c.	0 c.c.	1.0 KBr	10.5 c.c.	15.0 c.c.	10.5 c.c.	15.0 c.c.	10.5 c.c.	15.0 c.c.
		1.0 KI 0-1	0.0 "	0.0 "	3.0 "	3.0 "	6.0 "	6.0 "
		10% gelatin	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "	50.0 "
		Water	10.5 "	6.0 "	4.5 "	3.0 "	4.5 "	0.0 "

First digestion, (a) 10'/50°C (b) 120'/50°C.
 Standing in ice box, (a) one day (b) 3 days.
 Second digestion, (a) 10'/50°C (b) 120'/50°C (c) 180'/50°C.

The exposure for the sensitometry was 1 c.p. 1 meter 15 secs. and the development was for 10 mins. at 15°C. The sensitivity is shown in Tables 31, 32 and 33.

Two of these three tables were compiled only by rearrangement of the other one to show the reseductive influence more clearly.

Table 31.

Influence of ammonia is seen in horizontal columns.
 Influence of first digestion is seen in vertical columns.

F	E	A	0.0						3.0						6.0					
		C D	10.5			15.0			10.5			15.0			10.5			15.0		
			2	5	10	2	5	10	2	5	10	2	5	10	2	5	10	2	5	10
10'	1	10' 120'	5 5	5 10	7 11	3 7	6 8	7 9	8 10	9 13	12 13	8 12	11 13	13 14	11 13	11 15	13 19	7 16	12 13	12 14
	3	10' 120'	4 4	7 7	10 9	3 6	4 7	6 8	4 12	8 15	10 15	6 11	8 12	10 14	5 11	11 13	12 16	5 12	7 12	10 14
120'	1	10' 120'	6 10	9 11	11 15	6 8	9 8	10 12	12 17	12 19	14 20	8 8	14 15	13 19	10 12	12 17	15 20	8 12	13 14	14 16
	3	10' 120'	7 9	10x 10	11x 13	3 8	6 9	7 8	11 14x	11 17x	12 18	7 12	11 16	14 17	11 14	14 17	15 19	7 11	8 13	11 15
180'	1	10' 120'	5 10	7 10	10 12	4 9	5 10	8 12	11x 15x	12x 17x	13 18	6 12	14 18	15 18	8x 14x	11x 17x	14x 19x	8 11	12 12	13 14
	3	10' 120'	8 10	11x 10	8x 12	3 8	7 10	10 8	10x 15x	10x 17x	13 18	10 12	14 16	14 19	10 14	15 17	15 18	8 8	10 12	11 14

A denotes molar percentage of AgI in AgBr.
 B denotes volume of 1.0 KBr used in each emulsion in c.c.
 C denotes volume of ammoniacal 1.0 AgNO₃ used in each emulsion in c.c.
 D denotes time of first digestion in mins.
 E denotes numbers of days allowed to stand in ice box.
 F denotes time of second digestion in mins.

Table 32.

Influence of AgI is seen in horizontal columns.

Influence of second digestion is seen in vertical columns.

D	E	C A F	2						5						10					
			10.5			15			10.5			15			10.5			15		
			0	3	6	0	3	6	0	3	6	0	3	6	0	3	6	0	3	6
10'	1	10'	5	8	11	3	9	11	7	12	13	3	8	7	6	11	12	7	13	12
		120'	6	12	10	9	12	12	11	14	15	6	8	8	9	14	13	10	13	14
		180'	5	11	8	7	12	11	8	13	14	4	6	8	5	14	12	8	15	13
10'	3	10'	4	4	5	7	8	11	10	10	12	3	6	5	4	8	7	6	10	10
		120'	7	11	11	10	11	14	11	12	15	3	7	7	6	11	8	7	14	11
		180'	8	10	10	11	10	15	8	13	15	3	10	8	7	14	10	10	14	11
120'	1	10'	5	10	13	10	14	15	11	13	16	7	12	16	8	13	13	9	14	14
		120'	10	17	12	11	19	17	15	20	20	8	8	11	8	15	14	12	19	16
		180'	10	15	14	10	17	17	12	18	19	9	12	11	10	18	12	12	18	14
120'	3	10'	4	12	11	7	15	13	9	15	19	6	11	12	7	12	12	8	14	14
		120'	9	14	14	9	17	17	13	18	19	8	12	11	9	16	13	8	17	15
		180'	10	15	14	10	17	17	12	18	18	8	12	8	10	16	12	8	17	14

Table 33.

Influence of KBr is seen in horizontal columns.

Influence of day of standing is seen in vertical columns.

F	D	A C B E	0.0						3.0						6.0					
			2		5		10		2		5		10		2		5		10	
			10.5	15	10.5	15	10.5	15	10.5	15	10.5	15	10.5	15	10.5	15	10.5	15	10.5	15
10'	1	10'	5	3	5	6	7	7	8	8	9	11	12	13	11	7	11	12	13	12
		3	4	3	7	4	10	6	4	9	8	8	10	10	5	5	11	7	12	10
10'	120'	10'	5	7	10	8	11	9	10	12	14	13	13	14	12	16	15	13	16	14
		3	4	6	7	7	9	8	12	11	15	12	15	14	11	12	13	12	16	14
120'	1	10'	6	6	9	9	11	10	12	8	14	14	14	13	10	8	12	13	15	14
		3	7	3	10	6	11	7	11	7	11	11	12	14	11	7	14	8	15	11
120'	120'	10'	10	8	11	8	15	12	17	8	19	15	20	19	12	12	17	14	20	16
		3	9	8	10	9	13	8	14	12	17	16	18	17	14	11	17	13	19	15
180'	1	10'	5	4	7	5	10	8	11	6	12	14	13	15	8	8	11	12	14	13
		3	8	3	11	7	8	10	10	10	10	14	13	14	10	8	15	10	15	11
180'	120'	10'	10	9	10	10	12	12	15	12	17	18	18	18	14	11	17	12	19	14
		3	10	8	10	10	12	8	15	12	17	18	18	17	14	8	17	12	18	14

From these results, the following facts are to be seen :

Table 31/horizontal columns : With only 5 exception in 72 cases, the more the ammonia used, the higher is the sensitivity obtained. From this result, it is known how important the presence of ammonia is for the high sensitivity of emulsions and its influence may be considered to be due to the coagulation and recrystallization of the precipitates as described before.

Table 31/vertical columns : With only 4 exceptions in 108 cases, the emulsions which were digested 120 mins. before washing show higher sensitivity than those with 10 mins. digestion and this influence may be considered to be due to the contact of sensitive nuclei with AgI or AgBr by the slow recrystallization through the gelatin layer within the grain as described before.

Table 32/horizontal columns : In 72 cases

36 cases, 3% AgI,	highest sensitivity
14 cases, 3% and 6% AgI,	equal sensitivity
22 cases, 6% AgI,	highest sensitivity

From this result, it is known how necessary the presence of a small amount of AgI in AgBr emulsion is for the high sensitivity of emulsions and its main function may be considered to be its action as halogen acceptor. The optimum percentage of AgI in AgBr seems to vary according to the other conditions.

Table 32/vertical columns : In 72 cases,

35 cases, 2nd. digestion 120 mins.,	highest sensitivity.
20 cases, 2nd. digestion 180 mins.,	highest sensitivity.
17 cases, 2nd. digestion 120 mins. and 180 mins.,	equal sensitivity.

The result shows the same fact as that by the digestion before washing shown in Table 31/vertical column. But it is known that over-digestion causes fog even in the slow recrystallization with no solvent except water and its cause may be attributed to the elimination of KBr from AgBr grains as described before.

Table 33/horizontal columns : In 108 cases,

63 cases, KBr 10.5 c.c.	higher sensitivity.
23 cases, KBr 15.0 c.c.	* higher sensitivity.
22 cases, KBr 10.5 c.c. and 15.0 c.c.	equal sensitivity.

From this result, it is known that the amount of excessive KBr should not be great in most cases but its optimum amount varies according to the other conditions.

The necessity of a certain amount of excessive KBr may be attributed to the protection against fog but the lowering of sensitivity by too great an amount of excessive KBr seems to be due partly to the excessive occlusion or adsorption of KBr by AgBr grains and partly to the loss of AgCl nuclei through their being converted into AgBr by KBr.

Table 33/vertical columns: In 108 cases,

65 cases, allowed to stand for one day	higher sensitivity.
23 cases, do. for 3 days	higher sensitivity.
20 cases, do. for one day and 3 day	equal sensitivity.

The result shows that allowing the emulsion to stand after the first digestion makes the sensitivity a little higher in some emulsions because the sensitivity of some of the emulsions which were allowed to stand for 3 days was higher than that of the ones stood for one day. The optimum time for emulsions to be allowed to stand seems to vary according to the nature of the emulsion. Finally, the crosses marks in Table 31 denote the emulsions which gave fog with 10 mins. development. It will be found in Table 31 that all of these fogging emulsions are limited to those which were prepared with only 10.5 c.c. of 1.0 KBr solution. Thus, the formation of fog has a close connection with the excessive amount of KBr as described before.

In brief, it is quite impossible to find any general laws from these results but they may serve to explain some features of the formation of emulsions.

(VIII) PROPERTIES OF AgBr EMULSIONS.

In this section, some of the properties of AgBr emulsion are explained mainly from the standpoint of the AgCl sensitive nuclei.

(A) Developability of AgBr grains.

The effect which appear in photographic negatives is the result not only that of light but also that of development, which is a purely chemical process occurring quite independently of light. Trivelli and Sheppard⁽³³⁾ concluded that the lack of parallelism between the visible sensitivity and the developable sensitivity is due to the independence of the visible sensitivity of the sensitive nuclei. But, the dependence of developable sensitivity on the developability of AgBr grains may be added as another cause for the lack of parallelism between them.

Now, in the preceding sections, the existence of a minute trace of AgCl nuclei within the AgBr grains was presumed on the basis that AgCl particles will be protected by AgBr particles against the attacking action of KBr solution both at their precipitation and at digestion. Then it must follow that for the same reason, the developing solution will not be able to diffuse into the grain at development to induce the reduction of AgBr at a development centre formed by the action of light in the central part of the grain. But the following observations may explain this problem in some degree.

A little precipitate of AgCl, AgBr and AgI was enclosed in a soft paraffin while hot and it was exposed to sun light at a temperature a little lower than that of melting point of the paraffin. After a long exposure, a minute bubble appeared from the AgCl within the paraffin, a little later from AgBr and at last from AgI, as shown in Figure 6. From this fact, it may be said that the pressure of the chlorine vapour within the AgBr grains at exposure must be fairly strong so that a small explosion of the AgBr grain at the AgCl nucleus within the grain may be imagined. Then, some destruction of the AgBr crystal may be expected from such an explosion at exposure. In fact, it was already observed in section (I) that a AgBr grain shows some visible collapse after a long exposure to light. From such a phenomenon occurring in the extreme case of long exposure, a minute crack at the point of the AgCl nucleus in the AgBr

(33) *J. Phys. Chem.*, **29** 1568 (1925).

grain may be imagined in the case of ordinary exposure. The bright points in AgBr grains which are seen by the aid of the ultramicroscope may be due not only to the metallic silver but also to the crack above described. But owing to the lack of resolving power in the ultramicroscope and the destruction of fine detail by the diffraction disc itself, it is difficult to find whether they are due only to the metallic silver or both to the silver and to the crack.

By the axial illumination, such cracks could not be found even with the objective with N.A. 1.4. At any rate, if the formation of such cracks is assumed from the result of the extreme case, the development may be considered to be accelerated by the diffusion of developing solution to a development centre through such cracks. The formation of a latent image by some chemicals⁽³⁴⁾ without exposure to light makes the above conception of the mechanism of development very doubtful. But it is another question whether the action of chemicals occurs really in sensitive nuclei within the grain as in the case of light or whether it affects only AgBr itself on its surface.

At all events, the mechanism of development by diffusion of developer through such cracks may be considered not to be the absolute one but only to be comparative. It is well known that there is no dry plate which does not fog at all after very long development without exposure. For example, with one hour of development, all kinds of dry plates give fog of fairly high density without exception. This may be explained as follows: When the plate with no exposure is soaked very long in the developing solution, the developer diffuses into the grain even with no crack and it reduces the AgCl nuclei first and then the reduction of the whole AgBr grain is induced by the silver produced from AgCl. On the contrary, when the plate containing latent image is soaked in developing solution, the reduction of the grain which has some cracks by the result of exposure begins long before the grain with no crack begins to be reduced.

The fogging of dry plates by mechanical scrubbing may be explained

(34) Namias: *J. Phys. Chem.*, **14** 326 (1910).

by assuming that the AgCl nuclei of AgBr grains is partly uncovered by the destruction of grains. The increase of sensitivity by preexposure to dim light may be explained by assuming that the AgCl nuclei are partly decomposed by it without giving no cracks i.e., without increasing any developability.

The action of optical sensitizer in which the plate is soaked only a few minutes in its solution seems to be also contradiction to the above conception of development because the sensitizer must be considered to reach the AgCl nuclei in such a short time. But it may be due to the diffusion of dye into the grain not only at the soaking but also at the drying of the plate. In brief, some further experimental evidence seem to be necessary to explain the connection between the existence of AgCl nuclei and the mechanism of development.

(B) Sensitivity and the size of AgBr grains.

It is well known that a high speed emulsion generally contains larger AgBr grains than one of slower speed⁽³⁵⁾.

The sensitive material of dry plates being taken as AgBr, the relation between the size of the grains and their sensitivity has been investigated by many authorities⁽³⁶⁾, and it has been completely established that there is no strict parallelism between the size of grain and their sensitivity. These relations may be explained from the standpoint of AgCl sensitive nuclei as follows: The first question is, why do high speed emulsions contain on the whole coarser grain?

Now, as was described in the preceding section, the association of the AgCl sensitive nuclei with AgI or AgBr at digestion, in other words, the ripening by the recrystallization within the grain is accompanied by the recrystallization of AgBr grains. Hence, it is obvious that the ripening of the emulsion and the recrystallization of AgBr grains proceed parallel in a certain limit of time so that the coarse grained emulsion will show on the whole the higher sensitivity. It may be also considered that the coarser

(35) Sheppard etc.: *J. Phys. Chem.*, **27** 1 (1923).

(36) Sheppard: *J. Phys. Chem.*, **27** 1 (1923).

Svedberg: *Z. wiss. Phot.*, **20** 36 (1920).

Ty: *Phot. Jour.*, **19** 417 (1921).

grain will show comparatively higher sensitivity in one and the same emulsion, because the coarser grain contains more AgCl nuclei and therefore more probability of the association of AgCl nuclei and AgI particles within the grain. The second question is why is there no strict parallelism between the size of a grain and its sensitivity? The rate of ripening within the grain may not be necessarily the same as that of the increase in grain size because these two rates obviously vary according to the composition of the grains and the conditions under which the emulsion is digested, so that the sensitivity and the size of a grain do not show any strict parallelism even in one and the same emulsion and especially in different emulsions. The grain size of an emulsion is connected not only with sensitivity itself but also with the range of sensitivity, as was shown by Mees⁽³⁷⁾, and with the shape of the plate curve, as was shown by Slade and Higson⁽³⁸⁾ and by Sheppard and his co-workers⁽³⁹⁾.

These connections seem to be very complicated, probably depending on one or more of the relations between the size of a grain and the sensitivity of an AgCl nucleus in the same grain, the developability of grains, the distribution of grain size in the emulsion and the phenomenon which occurs at development.

Lastly, it may be said that fine-grained high speed emulsions may be possible to be prepared if the condition at the precipitation of AgBr is suitably selected and then the emulsion is digested under the condition which does not much increase the size of AgBr grains.

(C) Spectral sensitivity of AgBr emulsion.

According to the result of Eggart and Schmidt⁽⁴⁰⁾, the spectral absorption of AgBr occurs in the region from ultraviolet to 480 millimicrons and that of AgCl in the region from ultraviolet to 400 millimicrons. On the other hand, the maximum of the spectral sensitivity of AgBr gelatin emulsions occurs generally⁽⁴¹⁾ in the neighbourhood of 450 millimicrons.

(37) *J. Frank. Inst.*, **193** 141 (1915).

(38) *Phot. Jour.*, **17** 260 (1919).

(39) *J. Phys. Chem.*, **27** 1 (1923) and its continuation.

(40) *Z. f. Physik.*, **46** 541 (1928).

(41) *Eder: Z. wiss. Phot.*, **24** 142 (1926).

From these facts, the sensitiveness of AgBr emulsions seems rather to depend on AgBr itself than on AgCl nuclei so that the existence of AgCl sensitive nuclei becomes very doubtful. But it is well known that the spectral sensitivity of sensitized plates appears always in the neighbourhood of the absorption spectra of the dye used for the sensitization and not of AgBr itself. Thus, it is obvious that the spectral sensitivity does not necessarily coincide with the absorption spectra of the sensitive material itself so that the great difference between the absorption spectra of AgCl and the spectral sensitivity of dry plates may not be a contradiction against the existence of AgCl sensitive nuclei. The matter may be explained as follows: The function of AgBr with regard to AgCl nuclei is not only to act as a halogen acceptor but also, it may be considered, to act analogously to an optical sensitizer. In other words, the absorption spectra of AgBr may affect the spectral sensitivity of AgCl nuclei, its region varying according to the content of AgBr or to the absorption spectra of AgBr.

The following result of experiment shows such an analogy between the action of an optical sensitizer and that of AgBr in some degree. The absorption spectra of various optical sensitizers were measured by the spectral densograph of Zeiss-Ikon and the spectral sensitivity of plates sensitized by these optical sensitizer was measured by the spectrograph, about 25 spectra being taken with varying exposures. The result is shown in Table 34.

Table 34.

Sensitizer	First maximum.			Seconed maximum.		
	Absorption	Sensitizing	Deviation	Absorption	Sensitizing	Deviation
Silver bromide	430—440	450	20—10	—	—	—
Pina chrom	565	590	35	528	545	17
Pina verdol	550	585	35	520	530	10
Dicyanin	650	645	35	610	580	25
Dicyanin A.	660	590	30	600	—	—
Krypt cyanin	695	740	45	625	—	—
Ortho-chrom T.	557	590	33	525	540	15
Pinacyanol	593	645	52	540	585	45

From this table, the analogy of AgBr to an optical sensitizer may

be seen because the deviation of the spectral sensitivity of sensitized plates from the spectral absorption of the respective sensitizers or from that of AgBr is not different on the whole. For the same reason, the variation in the spectral sensitivity of AgBr emulsions according to the content of AgI⁽⁴²⁾ may be explained by considering the function of AgI with regard to AgCl nuclei to be analogous to that of sensitizers.

The occurrence of only one maximum of spectral sensitivity in iodobromide emulsion or chloro-bromide emulsion⁽⁴³⁾ may be explained by considering AgI or AgBr as the optical sensitizer for AgCl.

There is another analogy between the action of AgBr or AgI and that of a sensitizer. That AgBr or AgI acts as a chlorine acceptor was stated in the preceding section and the same happens in the dyes which are used as sensitizers. If a dilute solution of an optical sensitizer is mixed with one drop of dilute solution of chlorine or bromine water, these two react violently, discharging the color of the dye at the same moment. From this fact also, the mechanism of the function of AgBr or AgI for AgCl nuclei may be considered to be the same as that of the sensitizers. In other words, the function both of the dyes and of AgBr or AgI with regard to AgCl nuclei may be explained as being to act both as chemical and as optical sensitizers.

(D) Why is AgBr used in dry plates?

In the preceding sections, it was found that AgCl containing a little AgI has the highest sensitivity both in visible darkening and in latent image formation at a certain case. In spite of this fact, the high speed plates in the present time are prepared from empirical knowledge with AgBr as the main body of the emulsions. The difference between the experimental result in such a case and the result of experience may be explained by the result shown in Table 23.

The sensitivity of AgCl emulsion containing a little AgI was found

(42) *Hiuse. Phot. Jour.*, **66** 306 (1924).

(43) *Eder's Handb.*, III (1903) p. 143.

to be lower than that of high speed commercial plates only on account of the fog formation though it is high than others if the emulsion is prepared under certain conditions.

The formation of fog in such an emulsion seems to be due to the existence of AgCl in too large amount, because pure AgCl emulsions are well known to have a strong tendency to fog. On the other hand, the AgI emulsion containing a little AgCl was found to be very low both in sensitivity and in density. The lack of sensitivity and density in such emulsions seems to be due to the small developability of AgI, because pure AgI emulsions always show the same property. Thus, the existence both of AgCl and of AgI in large amount in emulsions is not admissible on account of the fog formation or of the small developability.

For these reasons, the dilution of these two important silver halides (AgCl and AgI) by AgBr seems to be the best means to obtain high speed emulsions though this was found only by experience and had no experimental foundation.

But it may be added that the limitation of the sensitivity of AgCl emulsion containing a little AgI is due only to fog formation, and one of the causes of fog is the reduction potential of the developer. If the formation of fog in such an emulsion is regulated both by the conditions of the preparation of the emulsion and by the developer, it may not be impossible to obtain a new superior emulsion consisting of AgCl and a little AgI.

SUMMARY.

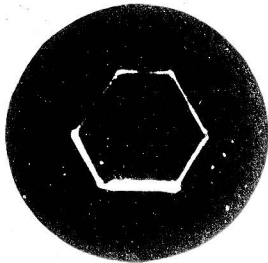
It is found by microscopic test that the occurrence of sensitive nuclei is a characteristic property of silver bromide, and silver bromide is accompanied by these nuclei at its precipitation even from aqueous solutions of precipitants. The nature of these sensitive nuclei in silver bromide crystals was presumed from the results of electrometric titration to be silver chloride which was precipitated from a minute trace of soluble chloride contained as an impurity in potassium bromide.

Further experiments have shown that silver bromide and silver iodide

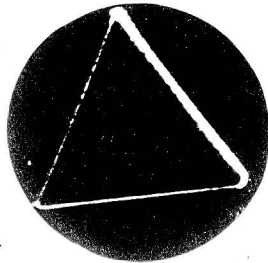
in photographic emulsions act as both chemical acceptor and optical sensitizer for silver chloride nuclei.

The ripening of an emulsion at digestion is explained by the coming in direct contact of silver chloride nuclei with silver bromide or iodide within the grain by diffusion through a thin layer of gelatin which was occluded at precipitation and isolates the silver chloride nuclei from other silver halides.

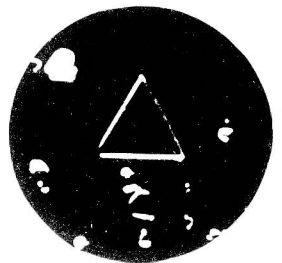
To sum up again, the sensitiveness of silver bromide plates is concluded to be due to the sensitiveness of silver chloride.



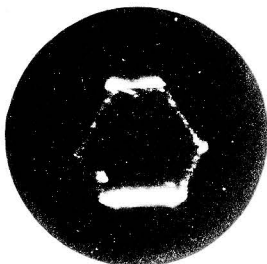
AgCl No. 1.



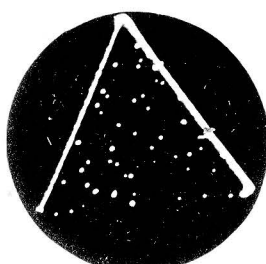
AgBr No. 1.



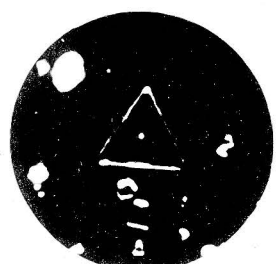
AgI No. 1.



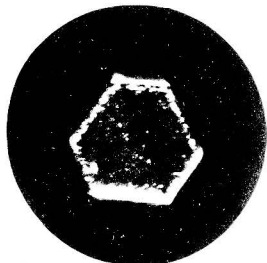
AgCl No. 2.



AgBr No. 2.



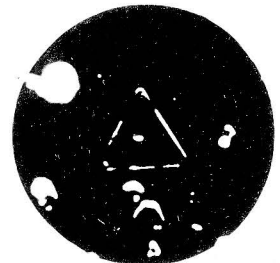
AgI No. 2.



AgCl No. 3.



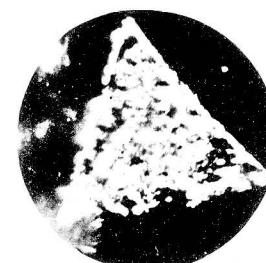
AgBr No. 3.



AgI No. 3.



AgCl No. 4.



AgBr No. 4.



AgI No. 4.

Fig. 1.

Fig. 2.

Fig. 3.

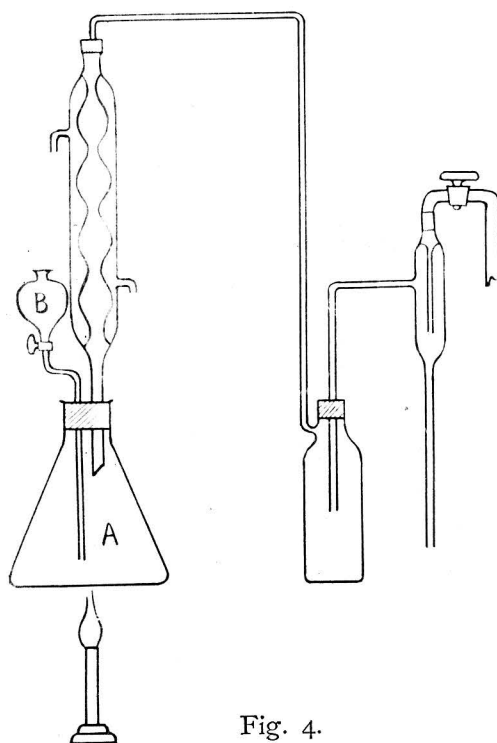
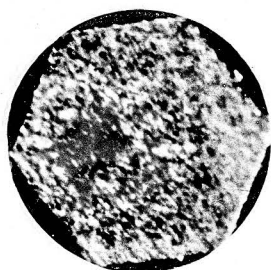
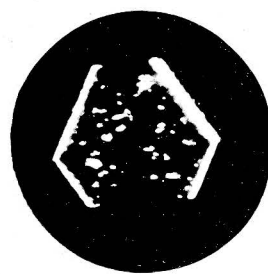


Fig. 4.



(a)



(b)

Fig. 5.

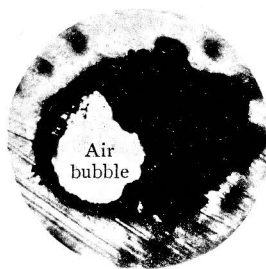


Fig. 6.