about 1.7 (excess silver) to 1.4 (excess bromide) times as great as on the aged products. It is not possible to say whether this is due to a changed orientation of the adsorbed dye or to other causes.

On the aged product 1 molecule of methylene blue was found to be adsorbed per 11.6 bromide ions on the surface. This value is in fair agreement with that reported by Wulff and Seidl[3] of 7.6 for a well-aged product the surface of which was measured microscopically and found to be about 2.5 times as great as that of our product E. The increased density of occupation of methylene blue on the fresh products has been explained above.

3. From a practical point of view the wool violet method either in an excess of silver or in an excess of bromide seems satisfactory for the determination of the specific surface of silver bromide of varying ages. The values found by the wool violet method are in satisfactory agreement with those found by the "w.v. r.a." method. In Table

TABLE VII

COMPARISON OF VARIOUS METHODS FOR DETERMINATION OF SPECIFIC SURFACE

	"r.a. W.V."	W.V. (Ag+)	W.V. (Br-)	"r.a. M.B."	M.B.
Surface B/ Surface E	47	77	64	73	104
Surface B/ Surface A	1.16	1.12	1.10		

VII is given the ratio of the specific surfaces of the products determined by different methods.

Summary

1. A rapid incorporation of radioactive bromide into well-aged silver bromide occurs when a solution of the former is shaken with the solid.

2. Adsorbed wool violet and methylene blue limit the exchange between solution and solid to the surface layer only. Use of this is made in the radioactive determination of the specific surface of fresh and aged products of silver bromide. Adsorbed gelatin inhibits the recrystallization of aged silver bromide.

3. Wool violet is found suitable for the determination of the specific surface of silver bromide. From a solution containing an excess of silver the amount of dye adsorbed is twice as great as that from a solution containing an excess of bromide.

4. The saturated surface of an aged product of silver bromide contained per 10.9 bromide ions 1 molecule of wool violet (excess Ag^+) or per 20.2 bromide ions 1 molecule of wool violet (excess Br^-), and per 11.6 bromide ions 1 molecule of methylene blue (excess Br^-). With a fresh product the following figures were found: 6.5, 14.5, and 5.2, respectively.

Studies on Aging and Formation of Precipitates. XXXI. The Aging of Silver Bromide

BY I. M. KOLTHOFF AND A. S. O'BRIEN[1]

In previous studies it has been found that fresh imperfect precipitates perfect themselves as a result of repeated recrystallizations which take place mainly in liquid films around the primary particles. Consequently, lattice material may deposit in interstices of an agglomerate of primary particles, thus cementing the latter together and causing a marked decrease of the specific surface of the precipitate.[2] The speed of this kind of aging was found to be determined by the solubility of the precipitate in the aging medium or more exactly in the liquid film around the particles. Ostwald ripening involving the growth

of large particles at the cost of small ones was found to be of secondary significance with regard to the type of aging discussed above.

In the present paper studies on the aging of freshly prepared silver bromide are reported. It was found again that the speed of aging increased with increasing solubility of the precipitate. However, when the solubility had reached a certain minimum value, further decrease of the solubility did not affect the still fairly large speed of aging. Evidence is given in this paper that this relatively rapid aging is due to a thermal aging of silver bromide which also occurs in the dry state even at room temperature.

In general the aging was followed by two methods: (a) by determining the decrease of the

(1) From a doctor's thesis submitted by Albert S. O'Brien to the Graduate School of the University of Minnesota, June, 1938.
(2) Compare S. E. Sheppard and R. H. Lambert, *Colloid Symposium Monograph*, 6, 276 (1928).

specific surface of the precipitate as indicated by the decrease of the amount of wool violet adsorbed on a saturated surface; (b) by determining the speed of exchange between radioactive bromide in solution and inactive bromide in the aging solid. This speed is governed by two factors: the specific surface and the degree of perfection of the precipitate. For this reason more comprehensive conclusions can be arrived at from the dye experiments.

For details regarding the radioactive experiments and the measurement of the wool violet adsorption reference is made to a previous paper.[3]

Experimental

Preparation of Silver Bromide and Study of Aging by the Dye Method.—The specific surface and other characteristics of the precipitate were found to depend upon the method of precipitation. By adopting a definite technique it was possible to obtain reproducible results. To weighed 120-ml. bottles each containing 25 ml. of 0.426 M silver nitrate and 0.5 ml. 0.1 M silver was added from a pipet in twenty-five seconds 25 ml. of 0.426 M potassium bromide. The bottles were swirled in a uniform manner during the precipitation of the 2.0 g. of silver bromide. The bottles were stoppered quickly, shaken vigorously by hand for fifteen seconds and the mother liquor which was 0.001 N in silver nitrate was decanted carefully. If the products were to be suspended in dilute silver nitrate solutions for aging, the precipitates were washed three times by decantation with 0.001 M silver nitrate. After completion of the washing the bottle was inverted carefully and allowed to drain, after which a convenient volume of aging solution was added. If the aging was to occur in dilute bromide solution, the precipitate was washed three times with water and once with 0.001 M bromide, and then it was treated as above. It was impossible to wash the fresh precipitate more than once with 0.001 M potassium bromide, as part of it would become peptized. After addition of the aging solution the bottles usually were placed on a mechanical shaker (200 phases per minute). After aging, a sufficient volume of a 0.1% wool violet solution was added to ensure a final dye concentration of 0.01 to 0.02% (saturated surface), and if necessary silver nitrate to give a final silver concentration of 0.001 M. The bottles were then replaced on the shaker for about one-half hour, weighed, and centrifuged until the supernatant liquids were perfectly clear. In an aliquot part of the latter, the dye concentration was determined with the aid of a photoelectric colorimeter and the amount of wool violet adsorbed per 1 g. of silver bromide calculated.

General Observations Regarding the Dye Adsorption.—Systematic investigations were carried out to determine the conditions under which the surface became saturated with wool violet. The results are given in a detailed and tabulated form in the thesis of the junior author[1]; they indicate that the surface was saturated when the silver concentration was greater than 0.0005 M and the final dye con-

(3) I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3409 (1939).

centration greater than 0.030 g. per liter. The amount of dye adsorbed did not change upon shaking for longer than fifteen to thirty minutes, indicating that adsorption equilibrium was obtained quickly and that no further aging occurred after the precipitate was covered with the dye. In all of the experiments the dye adsorption was determined from a solution which was 0.001 M in silver nitrate. Independent of the age of the precipitate it was found that the amount of dye on the saturated surface from a dye solution which contained an excess of bromide was one-half of that from a dye solution containing silver.

Air-dried samples were prepared and kept at room temperature in the dark for a week. Five grams of such a product was exposed for fifteen minutes to direct sunlight, the product being stirred repeatedly during the exposure. The product was dark gray after fifteen minutes, but adsorbed the same amount of wool violet (excess of silver) as the pure yellow unexposed sample. A sample of the gray product was exposed to bromine vapor, the excess of which was removed by a current of air. The product became completely yellow again and adsorbed the same amount of wool violet as before. These experiments show that a photochemical decomposition of the silver bromide does not affect the dye adsorption on the surface.

Aging of Silver Bromide. Wool Violet Method

Aging in Excess of Silver.—Experiments were carried out in which the fresh precipitate after washing was aged by shaking in 0.001 M silver nitrate for various periods of time. The results are given in Table I and also on curve 1 in Fig. 1. Even the fresh precipitate settles rapidly in an excess of silver nitrate. Sets of experiments comparable to those in Table I were carried out in which the precipitate was centrifugally packed before the aging, or in which the aging was carried out in 0.01 M silver nitrate or in a mixture which was 0.001 M in silver and 0.2 M in potassium nitrate. The results were the same as given in Table I.

TABLE I

AGING OF SILVER BROMIDE IN 0.001 N SILVER NITRATE

	Aged in 0.001 M AgNO$_3$ (shaken)		Centrifuged in 0.001 M AgNO$_3$ and allowed to stand
Time of aging	Wool violet adsorbed in mg. per g.	Br $\times$ 10^5 in equiv. on surface of 1 g. AgBr	Wool violet adsorbed in mg. per g.
5 min.	10.15	8.85	
15 min.			5.4
1 hr.	6.6	5.75	5.1
6 hrs.	3.3–3.6	2.9–3.1	
24 hrs.	3.05	2.65	2.9
2 days	2.2	1.9	1.9
1 week	1.4	1.2	
2 weeks	1.3	1.1	

Several experiments were made in which dye was added immediately after precipitation without removing the mother liquor. In this way it was found that the fresh precipitate adsorbed 15.9–16.0 mg. wool violet per gram, corresponding to 13.9–14.0 $\times$ 10^{-5} equivalent of bromide in the surface of 1 g. This tremendous surface development corresponds to 2.6% of all the bromide in the surface.

Aging in Excess of Bromide (0.001 M).—The results of experiments carried out under different conditions are

<div align="center">TABLE II</div>

SPEED OF AGING OF SILVER BROMIDE IN 0.001 M POTASSIUM BROMIDE UNDER VARYING CONDITIONS

Wool Violet in mg. adsorbed per 1 g. of silver bromide (satd. surface)

Time of aging, hr.	Shaken	Not shaken	Centrifuged, not shaken[a]	Centrifuged and shaken[b]	Aged in 0.2 M KNO$_3$ shaken[c]	Aged in 0.2 M KNO$_3$, not shaken	Centrifuged, aged in 0.2 M KNO$_3$, not shaken	Centrifuged, aged in 0.2 M KNO$_3$, shaken
$1/4$	3.5–3.6	2.8–3.1	2.7					
$1/2$	2.8–2.9		2.1–2.3		1.5; 1.5			
1	2.05–2.15		1.8	1.7–1.8	1.3–1.35	1.7–1.8	1.6; 1.6	1.3–1.4
6	1.35–1.40	1.65–1.75	1.30–1.40		0.80; 0.80	1.0–1.1	1.05; 1.05	0.8–0.9
24	0.8–0.9	1.25	1.1–1.25	0.4–0.5		0.60–0.70	0.8; 0.8	0.5; 0.5

[a] The precipitates after washing with water and 0.001 M bromide were shaken with the latter solution for two minutes, centrifuged for ten minutes at 2000 r. p. m. After centrifuging the samples were allowed to stand in a dark room for a given period of time. Then silver nitrate and wool violet were added, etc. [b] After centrifuging the samples were shaken during the aging. [c] After washing of the precipitates as above, they were suspended in a solution which was 0.001 M in bromide and 0.2 M in potassium nitrate and shaken during the aging.

<div align="center">TABLE III</div>

EFFECT OF EXCESS OF Ag$^+$ OR Br$^-$ ON FURTHER AGING OF SILVER BROMIDE

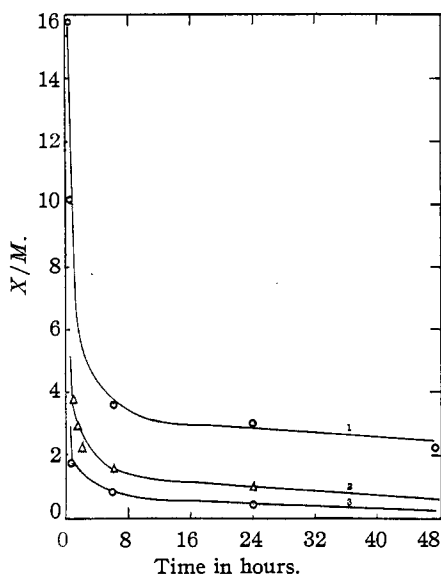|	15-Min. old product			6-Hr. old product	
Further aging in	Time of additional aging in min.	Wool violet adsorbed in mg. per g.	Further aging in	Time of additional aging in min.	Wool violet adsorbed in mg. per g.
		6.5–6.6			3.4–3.7
0.002 M Ag$^+$	15	6.05–6.05	0.005 M Ag$^+$	15	3.5–3.6
.002 M Br$^-$	15	4.0–4.2	.005 M Br$^-$	15	2.4–2.7

Fig. 1.—The aging of AgBr. Aging media: 1, 0.001 M AgNO$_3$; 2, 0.001 M KBr; 3, 0.001 M KBr, 0.2 M in KNO$_3$.

given in Table II; and some of them in Fig. 1. Comparison of Tables I and II (see also Fig. 1) shows that especially the initial speed of aging is much greater in 0.001 M bromide than in 0.001 M silver. It was of interest to study the effect of the silver and bromide concentration more systematically. In the first place experiments were carried out in which the fresh precipitate was aged in 0.1 M potassium bromide instead of 0.001 M solution. The fresh precipitate gave almost complete sol formation; after five minutes of shaking most of the precipitate had flocculated, while after fifteen minutes all of the precipitate settled

rapidly. After this period of aging the precipitate was washed rapidly and the dye adsorption was determined in 0.001 M silver under standard conditions. The precipitate adsorbed 1.18 to 1.26 mg. of wool violet per gram, while after aging for the same period in 0.001 M bromide the dye adsorption amounted to 3.5 to 3.6 mg. per g. If we realize that the fresh precipitate adsorbs 16.0 mg. wool violet per gram the tremendously rapid aging in excess of bromide becomes very striking.

Experiments were performed using 2-g. portions of carefully prepared fifteen-minute old, and six-hour old precipitates of silver bromide prepared from 0.3 M solutions which were further aged at varying silver or bromide concentrations. The results are given in Table III.

Finally, a set of experiments was performed in the following manner. Silver bromide was precipitated from 0.426 M solutions as described previously. Immediately after precipitation the pAg was adjusted to definite values (silver electrode in suspension) and kept as constant as possible. After aging for fifteen minutes silver nitrate was added to give a pAg of 3 and the adsorption of wool violet determined. The results are given in Table IV.

<div align="center">TABLE IV</div>

AGING OF FRESH PRECIPITATE FOR FIFTEEN MINUTES AT VARYING pAg(pBr)

pAg during aging	2	3	4	5	6	7	8	9
Wool violet adsorbed in mg. per. g.	11.7	11.7	8.8	5.9	5.0	3.9	3.0–3.1	2.5

At a pAg smaller than 3 the speed of aging did not further decrease, but with increasing pAg the rate of aging increased rapidly. The isoelectric point of fresh silver bromide was found to be located close to a pAg of 5, while the equivalence point is located close to a pAg of 6. At

values of pAg smaller than about 5 the precipitate contains adsorbed bromide.

Aging in Other Media.—In order to investigate the effect of the solubility of silver bromide in the aging medium, studies were made in which the fresh precipitate was kept suspended in various solvents. The results are given in Table V and graphically in Fig. 2. From the curves,

TABLE V

AGING OF SILVER BROMIDE IN VARIOUS MEDIA

Aging medium	Time of aging, hr.	Wool violet removed, %	Wool violet adsorbed in mg. per g.
0.001 M AgNO₃ in 1 M NH₃	1	1	<0.1
.001 M AgNO₃ in 1 M NH₃	6	0	< .1
.001 M AgNO₃ in 99%	1	47	7.0
ethanol	6	27	4.1
Benzene	20	25	2.5

it is seen that the speed of aging is of the same order in 0.001 M silver nitrate in water as in benzene. This made us suspect that under certain conditions the nature of the solvent did not play a part and that we were dealing with a thermal aging of the solid. In order to substantiate this conclusion, fresh samples of the precipitate were washed with water, ethanol and ether, after which air was drawn through until the odor of ether was no longer perceptible. Samples were then allowed to stand in dry bottles in a desiccator protected from light for given periods of time, after which the wool violet adsorption was determined. A comparison of the figures in Tables I and VI (see also curves 1 and 4 in Fig. 2) reveals that the surface decreases at about the same speed when the precipitate is kept in the dry state as when it is suspended in 0.001 M silver nitrate. It is to be expected that the speed of thermal aging will increase greatly with increasing temperature. Experiments were carried out, therefore, in which the precipitate was aged in dry bottles containing a trace of bromine vapor at 100°. The bromine was added to prevent the auto-decomposition of the fresh precipitate at 100°. When the latter was heated to 100°, in the dark a trace of bromine was developed and the surface became dark. When heated in the presence of a trace of bromine vapor the color of the precipitate did not change. After the heating, the samples were cooled and the trace of bromine was removed with a current of air before determining the adsorption of wool violet.

TABLE VI

AGING OF SILVER BROMIDE IN THE DRY STATE

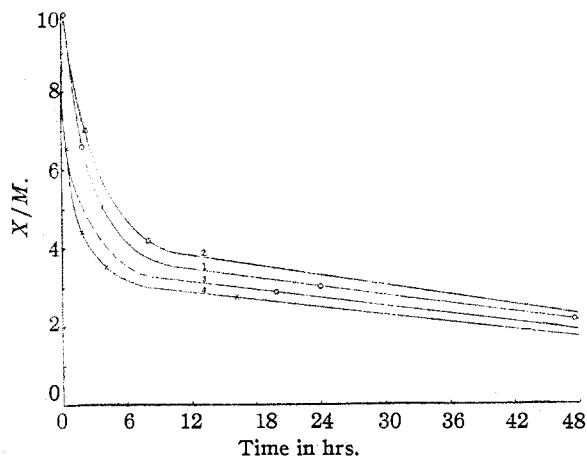| Time of aging	Aged at 25° Wool violet removed, %	Aged at 25° Wool violet adsorbed in mg. per g.	Aged at 100° Wool violet removed, %	Aged at 100° Wool violet adsorbed in mg. per g.
1/4 hour	66	6.6		
1/3 hour			41.5	2.3
1 hour			64.5	1.6
1.5 hours	58	4.4		
3.5 hours	68	3.4	68	1.3
17 hours	48	2.4	87	0.9
50 hours			26	.65
3 days	67–70	1.7–1.8		
7 days	53–55	1.05–1.1	0	.1
85 days	51	0.74		

Fig. 2.—Aging of silver bromide. Aging media: 1, 0.001 N AgNO₃ water; 2, 0.001 N AgNO₃ ethanol; 3, benzene; 4, air dried.

Qualitatively, the coarsening and perfection of the particles when aged in the dry state at room temperature can be shown by a decrease of the peptizability. When a 0.7-g. portion of the fresh air-dried product was shaken with 100 ml. of 0.01 M potassium bromide in a glass-stoppered graduated cylinder, about 80 to 90% of the solid settled out immediately; nevertheless the supernatant liquid consisted of an opaque yellow sol. When the solid was aged for twenty hours at room temperature the supernatant liquid obtained on shaking was only slightly turbid, while after aging for three months in the dry state none of the precipitate could be peptized in 0.01 M bromide.

Aging Studied by the Radioactive Method.—The speed of penetration of radioactive bromide when a solution of the latter was shaken with the solid was determined. Details regarding the experimental technique are given in a previous paper[3] and the thesis of the junior author.[1] Several 0.094-g. samples of silver bromide were prepared by adding 5 ml. of 0.102 M potassium bromide to 5 ml. of 0.1 M silver nitrate. Immediately after precipitation 10 ml. of a radioactive bromide solution of known composition was added and the mixture shaken for a given period of time. From the known activity and the bromide concentration of the mixture (0.0015 M) the number of equivalents of bromide ions exchanged per gram of silver bromide was calculated. The results are given in Table VII and in curve 1 of Fig. 3.

TABLE VII

SPEED OF PENETRATION OF RADIOACTIVE BROMIDE INTO FRESH SILVER BROMIDE

Time of shaking with Br,*ᵃ hr.	0.094-g. sample in 0.0015 M KBr Activity removed, %	0.094-g. sample in 0.0015 M KBr Equiv. Br⁻ × 10⁵ exchanged per g. AgBr[b]	0.47 g. sample in 0.1 M KBr Activity removed, %	0.47 g. sample in 0.1 M KBr Equiv. Br⁻ × 10⁵ exchanged per g. AgBr
1/4	80.5	219	54.4	506
1/2	86.6	345	58.4	598
1	92.5	653	60.4	659
2	92.7	675	62.0	691
4	93.0	696	63.0	725

ᵃ The asterisk denotes radioactive bromide.
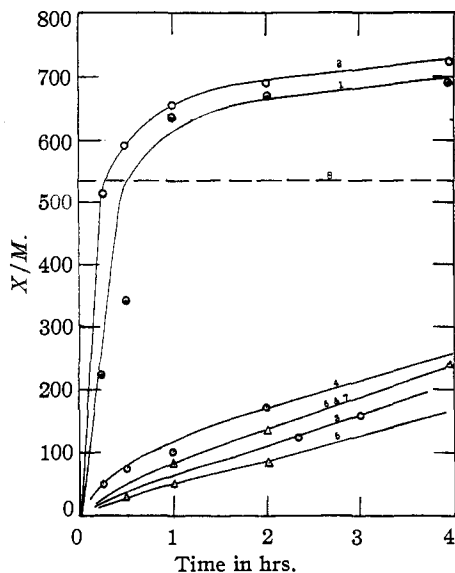ᵇ 1 g. AgBr contains 5.33 milliequivalents of bromide.

Fig. 3.—The rate of penetration of radio-active bromide ions in various AgBr precipitates: 1 and 2, fresh AgBr; 3, AgBr aged 2 hours in 0.001 M AgNO$_3$; 4, AgBr aged 2 hours in 0.001 M KBr; 5, AgBr aged 2 hours in 0.001 M KBr, 0.2 M in KNO$_3$; 6 and 7, fresh AgBr, with gelatin coating; 8, equilibrium value.

Another set of experiments was carried out with 0.47-g. samples which were washed quickly and shaken with 20 ml. of a radioactive solution which was 0.1 M in bromide (curve 2, Fig. 3). One gram of silver bromide contains 533 $\times$ 10^{-5} equivalent of bromide per gram, indicated by the dotted line in Fig. 3. Both fresh precipitates apparently are subject to very rapid recrystallizations. Within an hour of shaking the apparent amount of exchanged bromide is found greater than 100%, indicating the heterogeneous distribution of the active bromide through the precipitate during the early stages of aging. It is to be expected that the curves would show a maximum value after a longer time of shaking and then slowly would approach the point corresponding to homogeneous distribution of the radioactive bromide. The speed of penetration decreases very rapidly upon aging of the precipitate. Curve 3 of Fig. 3 (see also Table VIII) gives the time–penetration curve after aging of the precipitate represented by curve one for two hours in 0.001 M silver nitrate. Curve 4 of Fig. 3 refers to a precipitate (prepared as that of curve 1) which

TABLE VIII

SPEED OF PENETRATION OF RADIOACTIVE BROMIDE INTO SILVER BROMIDE AGED FOR 2 HOURS

Time of shaking with Br,* hr.	Aged in 0.001 M AgNO$_3$	Aged in 0.001 M KBr	Aged in 0.001 M KBr + 0.2 g. of KNO$_3$
$^1/_4$		46	19
$^1/_3$	33		
$^1/_2$		61	38
1		101	56
2	121 (2$^1/_3$ hrs.)	178	88
3	165		

had been aged by shaking for two hours in 10 ml. of 0.001 M potassium bromide. At the end of this period 0.2 g. potassium nitrate and 10 ml. of a radioactive bromide solution were added and the speed of penetration was determined.

A similar experiment was carried out in which the aging occurred in 0.001 M potassium bromide containing the potassium nitrate (curve 5, Fig. 3). The aging is found to be more pronounced in the presence of potassium nitrate; a result in agreement with that obtained from the experiments with wool violet.

Speed of Penetration in the Presence of Gelatin.—In a previous paper[3] it was shown that adsorbed gelatin prevented or at least inhibited the penetration of radioactive bromide into aged silver bromide and that, practically speaking, only exchange with bromide ions in the surface layer occurred. The following experiments show that gelatin inhibits but does not prevent the penetration of radioactive bromide into fresh silver bromide when the latter is shaken with a solution of the former. Samples of precipitates (0.094 g.) were prepared from 0.1 M solution (excess of Br 0.001 M). Immediately after precipitation 10 mg. of gelatin dissolved in 4 ml. 0.001 M bromide was added and the bottle shaken for ten minutes. Ten ml. of r. a. bromide solution (0.0039 M in bromide) was added and the mixture shaken. Similar experiments were carried out with 1 mg. instead of 10 mg. of gelatin. The number of equivalents of Br exchanged $\times$ 10^5 in the presence of 10 mg. of gelatin were 85, 135, and 244 after one, two, and four hours of shaking, and in the presence of 1 mg. of gelatin 98 and 164 after one and three hours of shaking. From these results and the curves 6 and 7 in Fig. 3 it is evident that adsorbed gelatin does not prevent the recrystallization and perfection of fresh silver bromide. It is of interest to mention that the effect of 10 mg. of gelatin was found to be the same as that of 1 mg.

Discussion

1. The speed of aging in 0.001 M bromide was found to be much greater than in 0.001 M silver nitrate, it increased with increasing bromide concentrations, but increasing concentration of silver was of no further consequence. The great effect of an excess of bromide is attributed to an adsorption of this ion which gives rise to the formation of argento bromide ions in the liquid film around the particles, resulting in an increased solubility and speed of recrystallization of silver bromide in the liquid jackets.[4] The rate of aging in an excess of silver was not found to be affected by the presence of potassium nitrate by shaking and by other factors. On the other hand, shaking and the presence of salt had a distinct effect upon the aging in an excess of bromide (see Table II and Fig. 1). This is attributed by us to a colloidal solution. Upon longer periods of aging, the suspensions which had been shaken had aged

(4) Compare I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, **59**, 1634 (1937).

more than those which had been allowed to stand. This effect is easily explained by an Ostwald ripening which will be much more rapid in the shaken than in the unshaken suspension. The aging in excess of bromide was strongly promoted by the presence of potassium nitrate in a concentration of 0.2 M. The salt flocculates the sol, the number of particles in an agglomerate being dependent upon the concentration and kind of flocculating electrolyte. It seems to us that another factor, namely, the distance of approach of the particles in the agglomerate may be of primary importance in connection with the aging. When the particles are close together less recrystallization is necessary to cause cementing than when the particles are farther apart. We have indication that the distance of approach becomes smaller with increasing concentration of flocculating electrolyte and with increasing flocculating power. In order to test this point, experiments were carried out in which to the fresh suspension of silver bromide in 0.001 M potassium bromide, aluminum nitrate was added in a concentration of 0.0004 M and 0.001 M, respectively. After half an hour of shaking followed by removal of the aluminum the amount of wool violet adsorbed per gram was 1.9 mg. (0.0004 M Al) and 1.5 mg. (0.001 M), respectively, while in the absence of aluminum this amount was 2.8 to 2.9 mg.

2. An increase of the solubility of the precipitate by the addition of ammonia increases the rate of aging. The most striking result of this study is that, when the solubility has reached a minimum value, the rate of aging no longer depends upon the solubility of the precipitate in the aging medium. Then, it was found that the rate of aging was practically equal in aqueous and ethanolic 0.001 M silver nitrate, in pure benzene, and in the air-dried state. Apparently, under the latter conditions the aging cannot occur by recrystallization by way of solution but in the solid itself. Fresh products of silver bromide are extremely imperfect and have a tremendous surface development (2–3% is surface), and, consequently, they have a very large active surface. Silver bromide molecules located on the latter are much richer in energy

than those on normal surface which in turn are richer in energy than those within the lattice. The thermal mobility of well-aged silver bromide is very small but that of our fresh products is quite pronounced. This is substantiated by the following experiments.[5] When fresh air-dried silver bromide is shaken with a solution of radioactive bromine in ethyl bromide or with anhydrous vapors of r. a. bromine, a rapid exchange between the radioactive bromine and the inactive bromide in the silver bromide occurs, resulting in a heterogeneous distribution of the active constituent through the solid. The speed of exchange decreased rapidly with increasing age of the precipitate.

Moreover, we found that fresh silver bromide has a relatively large electrical conductivity which, partly at least, is ionic. The properties of fresh bromide seem to be quite abnormal and it is planned to study the physical and also the chemical properties of such products in greater detail in the near future.

Summary

1. The rate of aging of silver bromide is much greater in a medium containing an excess of bromide than of silver, and it increases with the bromide concentration of the solution.

2. The colloidal state of the precipitate in an excess of bromide is of importance with regard to the speed of aging.

3. The effect of shaking upon aging indicates that upon longer periods of aging in a liquid medium of suitable solving power a slight Ostwald ripening occurs.

4. Adsorbed gelatin does not prevent the penetration of radioactive bromide into fresh silver bromide.

5. When the solubility of the silver bromide in the aging medium has reached a minimum value, recrystallization by way of solution becomes of no consequence. It is shown that fresh silver bromide is subject to a rapid thermal aging in the dry state, even at room temperature.

(5) I. M. Kolthoff and A. S. O'Brien, J. Chem. Phys., 7, 401 (1939).