num from iridium, a quantity of iridium less than 0.1 mg. was detected, in one experiment, in the filtrates obtained from the precipitation of platinum, first by hydrogen sulfide and then by formic acid, whereas no iridium was detected in the two other experiments.

In order to ascertain, in the separation of ruthenium by the recommended procedure, whether any of the other platinum metals reached the absorbing solutions, the ruthenium recovered from each of the three complete analyses was examined spectrochemically by Bourdon F. Scribner for osmium, platinum, palladium, rhodium and iridium, but no trace of these metals was detected.

The results of 31 experiments are given in Table I. Those reported in Nos. 1 to 24, inclusive, are taken from previous publications cited in this paper. Experiments Nos. 25 to 29, inclusive, were conducted according to the recommended procedure, except that brom cresol purple was used to determine the end-point for the hydrolytic precipitation. In these experiments some palladium escaped precipitation and was subsequently separated from the platinum by means of dimethylglyoxime. The results in Nos. 30 and 31 were obtained by following the procedure as herein written. Although osmium and ruthenium were not included, the solutions were, nevertheless, subjected to the same treatment as if they had been present, except that the distilling operations were omitted, in order to duplicate conditions which normally obtain at the end of the ruthenium distillation. In these two experiments, rhodium and iridium were not separated from each other but were recovered together by hydrolytic precipitation. The mixed precipitate was washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (*p*H 7), and ignited to a mixture of metallic rhodium and iridium. The final filtrates obtained in these two experiments were found to be free from the four metals concerned.

The quantities of metal listed in the table can be conveniently handled, analytically. In the case of platinum, 2 g. of this metal is easily handled, and 5 g. should introduce no difficulties.

Summary

1. A new and reliable procedure is described for the separation, recovery and determination of each of the six platinum metals.

2. The accuracy of this new method is comparable to that of the best analytical procedures for the common metals. No special equipment or reagents are necessary and the operations do not involve technique unfamiliar to a trained analyst.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Structural Changes Taking Place upon Aging of Freshly Prepared Crystalline Precipitates. V. The Thermal Aging of Freshly Prepared Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In papers III and IV of this series[1] it has been shown that the rapid internal perfection of the crystalline particles of freshly precipitated lead sulfate on aging in the supernatant mother liquor at room temperature is to be attributed to a rapid recrystallization process by way of the solution[2] and not to a free mobility of the lead ions in the amicronic particles within the microcrystals as originally concluded from the results reported in papers I and II.[3] Aside from the aging in liquid media it appears reasonable to expect that aging will occur in the dry state as well, provided that the fresh precipitate is heated to temperatures high enough to increase the thermal energy of the ions at the active surface. The results of this study are reported in this paper.

We may distinguish between two principal types of thermal aging.

1. **Microscopic Aging.**—At the higher temperatures a *sintering* of the microscopic particles may occur, resulting in a decrease of the external surface. The magnitude of this surface can be determined from the dimensions of the particles as seen with a microscope. Since the precipitates used in these studies were highly heterodisperse,

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[1] THIS JOURNAL, 57, 597, 607 (1935).

[2] This matter will be dealt with in detail in a subsequent paper of this series.

[3] THIS JOURNAL, 56, 1264, 1658 (1934).

more accurate results were obtained by calculating the external surface from the amount of wool violet adsorbed on shaking the crystals with a solution of the dye of a concentration sufficient to assure a saturated surface layer.[4]

2. **Internal Aging.**—At temperatures much lower than where the sintering takes place, an internal aging may occur, resulting in an internal perfection of the microscopic crystals. An indication of the extent of this kind of aging was obtained from the speed with which thorium B distributes itself through the precipitate.[1,3]

Experimental

Preparation of Lead Sulfate Samples.—A main supply of 70 g. of fresh lead sulfate was prepared by fairly slow precipitation at a speed which approximated the rate of formation of earlier samples.[1] To avoid excessive aging when in contact with the supernatant liquid, the precipitate was prepared in 3-g. batches by adding 98.6 ml. of 0.1 M potassium sulfate to 103.5 ml. of 0.1 M lead nitrate solution, while stirring with an electrically driven stirrer. Immediately after precipitation each portion of precipitate was filtered on a Gooch crucible, washed rapidly (suction) with water and absolute ethanol, and then air-dried.[1a] The precipitates thus obtained from the different batches were mixed and kept in a desiccator over sulfuric acid at room temperature. From previous investigations[3] it was known that under such conditions a fresh precipitate remains practically unaged. However, to eliminate any uncertainty, blanks were run on the dye adsorption and the Th B exchange at frequent intervals throughout the investigation. For the sake of brevity these results will not be reported since it appeared that within the given periods of time no distinct aging could be detected in the product stored at room temperature. Various other batches of lead sulfate prepared in a similar way were used to ascertain the validity of all effects encountered.

Adsorption of Wool Violet.—Eight-tenths to one-gram portions of lead sulfate were shaken for thirty minutes with 25 ml. of a wool violet solution containing 250 mg. of the dye and 40 mg. of lead sulfate per liter. It was shown that at this dye concentration the surface of the lead sulfate was saturated with wool violet, since the same amount of dye was adsorbed when the concentration in solution was increased to 350 and 500 mg. per liter, respectively. The quantity of wool violet left in the solution after shaking and centrifuging was determined colorimetrically in an aliquot part of the supernatant liquid. All determinations were run in duplicate at least and the average result is reported.

Exchange with Thorium B.—Exactly the same technique was followed as described in previous papers.[1,3] Approximately 0.3-g. portions of lead sulfate were shaken with 23.53 ml. of a solution of thorium B containing 0.00162 mole of lead nitrate and 0.065 mole of potassium nitrate per liter, corresponding to the composition of the solution in previous work.[1,3] Samples were shaken in paraffined containers for fifteen minutes and three hours and portions of supernatant liquid were withdrawn with a paraffined pipet after centrifuging. All determinations were made in duplicate at least and the average value is reported.

It should be realized that the reproducibility with unaged or slightly aged precipitates, especially after fifteen minutes of shaking, is not very good. Great accuracy is hardly to be expected under these conditions, since the thorium B distributes itself very quickly, and a slight change in the experimental conditions may have a marked effect. For the reasons mentioned, slight changes found in the amounts of lead exchanged do not indicate a definite aging. Such experimental errors are insignificant in comparison with the magnitude of the effects reported.

Losses in Weight of the Samples During Heating.—Weighed samples (varying between 5 and 10 g.) of the air-dried lead sulfate were placed in wide weighing bottles and heated at different temperatures in an electric oven, the temperature of which could be kept constant within 5°. At noted intervals of time the bottles were removed, cooled in a sulfuric acid desiccator and weighed with ground glass covers in place. The losses in weight were found to be very small: at 105° after two hours of heating 0.02%, after twenty-seven hours 0.03%; at 200° after two and one-half hours 0.08%, after twenty-eight hours 0.095%; at 250° after one hour 0.12%, after four hours 0.14%, after twenty-seven hours 0.15%; at 305° after one-half hour 0.14%, after three hours 0.18%, after twenty hours 0.25%; at 400° after one hour 0.24%, after four hours 0.29%; after twenty-seven hours 0.46%. Since the losses in weight were very small, a more elaborate and accurate study is desirable with regard to their proper interpretation.

The results obtained in the study of the microscopic and internal aging on heating of the fresh precipitate are summarized in Table I.

TABLE I

THERMAL AGING OF LEAD SULFATE

Temp. of heating, °C.	Time of heating, hours	Wool violet adsorbed in mg./1 g. of $PbSO_4$	Lead exchanged in mg./1 g. $PbSO_4$ after shaking with Th B for	
			15 minutes	3 hours
Unheated	..	1.45	38–45	600–800
105	2	..	33	790
105	27	1.57	25	800
200	2.5	..	39	780
200	27	1.60	*4.3*	*39*
250	1.2	..	*15*	*40–60*
250	4	..	*5.5*	20
250	27	1.40	*2.4*	7.2
305	0.5	..	17	110
305	1.2	1.56	13	92
305	3	..	17	70
305	20	1.19	10–15	61
400	1	1.10	16	76
400	4	..	7	18
400	27	0.39	8	17

Discussion

1. The results show clearly the difference between the external and the internal aging. On heating the fresh lead sulfate to temperatures

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(4) THIS JOURNAL, 56, 832 (1934).

between 100 and 200° and even for short periods to 305°, a slight but definite increase of the external surface was found as indicated by the increase of the adsorption of wool violet. This might be attributed to a slight decrepitation of the precipitate which in the fresh form is highly porous. From the figures given in the third column of the table it follows definitely that no sintering occurs at temperatures below 250°, and even after heating for twenty-seven hours at 250° there was only a very slight decrease of the external surface. The sintering becomes more pronounced but is still very slow upon heating at 300°. After heating for one hour at this temperature no indication of sintering was found, but it was very definite after twenty hours of heating at this temperature. At 400° the sintering became very pronounced, even after one hour of heating. After twenty-seven hours at this temperature the total external surface as measured by the wool violet adsorption had decreased about four times.

2. The internal aging occurs at much lower temperatures than the microscopic sintering. Thus it is evident from the data that after heating for twenty-seven hours at 200° a marked aging had occurred. On the other hand, after heating for two and one-half hours at this temperature there was no indication of an internal aging. From this behavior one would infer that there is a certain incubation period before the perfection starts. A drastic aging was found on heating to 250°, the fresh samples appearing quite "old" after having been kept for twenty-seven hours at this temperature. Apparently it is possible to perfect crystals of lead sulfate by heating to temperatures far below the sintering temperature. This conclusion will be substantiated by x-ray studies.

3. The internal aging of fresh lead sulfate at temperatures far below the sintering temperature may be compared with that of the various active catalysts, which show a marked decrease of catalytic activity when heated to considerably below sintering temperatures.[5] It has been shown[1,3] that our fresh precipitates are porous and have a large internal surface development. The mobility of the ions at the active surface will be greater than that of the ions in the inside of the normal lattice, where they are completely surrounded by lattice ions of opposite electrical charge. In the terminology of I. Langmuir and of Taylor,[6] the heat of evaporation of the ions will decrease as they become less saturated with neighboring ions. Langmuir and Taylor concluded that the rate of evaporation will fall off exponentially as the number of atom linkages increases. The thermal aging is thus attributed to a high mobility of lattice ions on the active surface, these ions moving to less active surface spots, resulting in a perfection of the crystals.

According to the above it is to be expected that after a certain time of heating at a given temperature a final state of perfection corresponding to that particular temperature will be found. In order to obtain a further aging the temperature has to be raised. From the results in Table I it is seen that virtually a final state of perfection is reached after heating for three hours at 305°. At 400° a much more drastic aging is found, a final state being reached after about four hours of heating. The experiments have been repeated with four different batches of lead sulfate, yielding qualitatively the same results. Incidentally it may be mentioned that during the thermal aging the crystals become more compact and less porous as indicated by their decreasing capacity of absorbing water when kept at room temperature at a relative humidity of 0.85 after the heating.

4. *The most striking and unexpected result of this study is that, upon heating at 250°, a much more pronounced aging was obtained than when heated at 300° and even at 400° for the same length of time.* A precipitate heated for twenty-seven hours at 400° behaved as though it were less aged internally than when heated for the same period at 250°, in spite of the fact that in the former case a pronounced sintering had occurred. Moreover it is of great interest to notice that the extent of aging at 250° depends upon the duration of heating, and that no final state was reached even after twenty-seven hours. At 300 and at 400°, on the other hand, maximum aging is attained after several hours.

From experiments reported in Table II it is seen that no further aging occurs at 305°, once the fresh lead sulfate has been heated for twenty-four hours at 250°. On the other hand, a 305° sample can be further aged at 250°. A new batch of lead sulfate different from that used in the experiments of Table I was used. Clearly, aging at 250° is more effective than at 305°.

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(5) For a review see H. S. Taylor, *J. Phys. Chem.*, **28**, 897 (1924).

(6) See H. S. Taylor, *ibid.*, **30**, 145 (esp. p. 162) (1926).

TABLE II

Treatment of sample	Lead exchanged in mg./ 1 g. $PbSO_4$ 15 min.	3 hours
24 hours at 250°	3.1	14.1
30 minutes at 305°	6.3	26.7
20 hours at 305°	9.0	23.5
24 hours at 250°, then 0.5 hour at 305°	3.3	12.6
24 hours at 250°, then 20 hours at 305°	4.7	14.7

It was thought at first that lead nitrate coprecipitated with lead sulfate during precipitation might be responsible for the peculiar results. It was thought possible that coprecipitated lead nitrate might decompose at temperatures of 300° and above. The lead oxide formed might then be able to protect the crystals from further aging. In order to test this point the nitrate content in the fresh product and after heating for twenty-four hours at 105, 200, 250, 305 and 400° was determined. The samples were decomposed with sodium carbonate solution and the nitrate in the filtrate measured colorimetrically according to the procedure developed by Kolthoff and Noponen.[7] It was shown that no decomposition of the coprecipitated nitrate occurred at temperatures of 300° and below, whereas the greatest part of the nitrate was removed after heating for twenty-four hours at 400°. In addition it was shown that no nitrite was formed after heating to temperatures of 300° and below. Hence the coprecipitated lead nitrate is not responsible for the fact that less aging is found when samples are heated for long periods of time at 300 to 400° than at 250° and even at 200°.

The only other impurity present in the lead sulfate is water in the adsorbed and occluded state. (See losses in weight upon heating, reported earlier in this paper.) Water present in the adsorbed state may promote the thermal aging of lead sulfate. There are indications that the adsorbed water is not removed at 250°, but is removed at temperatures of 300° and above. The presence of such a film of adsorbed water could be responsible for certain of the observations being reported, *i. e.*, that a continuous aging is found at a temperature of 250°, and that the aging is much more pronounced after longer times of heating at 250 than at 300° and even at 400°. From the results recorded in Table III it is quite evident that the coprecipitated water is responsible for the continuous and drastic aging at 250°. A new batch of fresh lead sulfate was prepared for these experiments. Duplicate samples were heated for varying times at 305°. One of the samples was removed from the oven, while the other was left in the oven and the temperature quickly readjusted to 250°. The heating was then continued at this temperature. After cooling, the exchange with Th B solutions was determined in the usual way. In addition the adsorption of wool violet was measured.

TABLE III

AGING OF LEAD SULFATE WHEN FIRST HEATED TO 305° AND THEN AT 250°

Treatment of sample	Lead exchanged in mg./ 1 g. $PbSO_4$ after shaking with Th B for 15 min.	3 hours	Wool violet adsorbed in mg./1 g. $PbSO_4$
2 hours at 305°	8.7	59	1.75
2 hours at 305°, then 24 hrs. at 250°	7.7	30	1.7
45 hours at 250°	2.9	8.2	1.75
21 hours at 305°	7.3	23	1.45
21 hours at 305°, then 21 hrs. at 250°	6.7	23	1.4

The last two results given in Table III are especially conclusive. Once the lead sulfate had been heated for twenty-one hours at 305°, no further aging occurred if the sample was maintained for twenty-one hours at 250°, and provided the solid had not been removed from the furnace. The final product remained fresher than when heated for twenty-one hours at 250° only. Apparently long periods of heating at 305° cause the removal of adsorbed and occluded water.

That the water actually is responsible for the continuous aging at 250° was shown conclusively by the following experiment. A sample of the fresh lead sulfate was heated for twenty-one hours at 305°, then for twenty-one hours at 250°, and finally cooled and placed in a desiccator over a deliquescent sodium sulfate decahydrate for a week. A similar sample was kept for the same time over concentrated sulfuric acid. Both samples were heated again at 250° for twenty-one hours. The amounts of lead exchanged after the final heating after fifteen minutes and three hours of shaking at room temperature were 1.0 and 7.3 mg., respectively, for the sample which had been stored over deliquescent sodium sulfate and 5.0 and 26 mg., respectively, for the sample kept over sulfuric acid.

The experiments reported in Table III have been repeated with a number of different batches

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[7] I. M. Kolthoff and G. Noponen, THIS JOURNAL, **55**, 1448 (1933).

of lead sulfate. All conclusions drawn from these abbreviated data have been substantiated by experiments with each independently prepared batch.

Summary

Fresh lead sulfate appears to undergo three distinct types of thermal aging.

1. *Microscopic aging by a sintering of the particles.* A pronounced sintering has been found at temperatures of 400°, and a very slow sintering at 300°.

2. *Internal thermal aging* at temperatures far below that of sintering. This aging is attributed to the high speed of evaporation of lattice ions on the active surface (Taylor and Langmuir). After a sufficiently long heating period the "age" approaches a final state which is characteristic for each temperature.

3. *Thermal aging promoted by adsorbed and occluded water.* This aging occurs at temperatures below the point where internal aging begins. It proceeds continuously with the time of heating. It accounts for the much more pronounced perfection after heating for twenty hours at 250° than after the same time of heating at 305 and 400°.

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Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. VI. The Perfection and Aging of Lead Sulfate Precipitated under Various Conditions

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In previous studies the aging of fresh lead sulfate obtained by mixing 0.1 *M* solutions of lead nitrate and potassium sulfate has been reported. In the present study, the effect of varying conditions of precipitation upon the perfection and the speed of aging of lead sulfate has been investigated.

Designation of the Various Precipitates of Lead Sulfate

1. **Lead Sulfate from 0.025 M Solutions.**—To 103.6 cc. of 0.025 *M* lead nitrate, 98.6 cc. of 0.025 *M* potassium sulfate was added in about five or six minutes. Four such precipitations were performed and the four portions of solid combined. The precipitate formed slowly, about half a minute being required before it appeared. One minute after the addition of the sulfate, the precipitate was filtered on a Büchner funnel, and treated further as sample 2. The "fresh" precipitate was thirteen to fourteen minutes old after washing with alcohol. Another sample was prepared by gently rotating the precipitate in the supernatant liquid for an hour before filtration.

2. **Lead sulfate from 0.1 M solutions** was prepared as described in a previous paper.[1]

3. **Lead Sulfate from 0.4 M Solution.**—To 53 cc. of 0.4 *M* lead nitrate was added 50 cc. of 0.4 *M* potassium sulfate while stirring. After the precipitation was complete, half of the suspension was decanted and placed in a rotatory shaker for one hour. The remainder was filtered immediately, washed with four 20-cc. portions of water, then with alcohol and finally air-dried. The fraction of the precipitate which had been shaken for one hour was treated in a similar way. Both the filtration and the washing process were rather slow, because the fine precipitate tended to cake on the filter and clog it. The "fresh" precipitate after the washing with water was twenty-four to twenty-five minutes old.

4. **Lead Sulfate from Extremely Dilute Solutions.**[2]—To 25 cc. of conductivity water were added simultaneously and dropwise from two dropping pipets 50 cc. of 0.1 *M* lead nitrate and 50 cc. of 0.1 *M* potassium sulfate, the suspension being stirred continuously during the precipitation. The precipitate which settled readily was filtered, washed and air-dried. The "fresh" precipitate was twelve minutes old.

5. **Lead Sulfate from 0.1 M Solutions at Boiling Temperature.**—To 103.6 cc. of 0.1 *M* lead nitrate heated to boiling was added in about five to six minutes 98.6 cc. of 0.1 *M* potassium sulfate solution at a temperature of about 95–100°. After precipitation, half of the suspension was decanted and placed on a rotatory shaker for

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[1] THIS JOURNAL, **56**, 1264 (1934) [Procedure A 1].

[2] F. Hahn, *Z. anorg. allgem. Chem.*, **126**, 257 (1923).