SOME EXPERIMENTS ON ALLOYS OF SILVER WITH
EMBRITTLING METALS.

Made at the United States Mint, Philadelphia,

BY

ALEXANDER E. OUTERBRIDGE, JR.

It is a fact very well known to metallurgists that the presence of certain base metals in refined gold and silver, even in such small percentages as to render their detection difficult, if not impracticable, by ordinary chemical tests, will nevertheless exercise such an injurious effect in regard to ductility, hardness, etc., as to render the metal totally unfit for coin or the industrial arts, thereby necessitating the removal of these impurities by oxidizing fluxes, or other equivalent means.

It is also well established that during the process of removing these impurities (technically called "toughening"), an inevitable, though variable, loss occurs.

This loss may be directly traced to three causes:

First. To the formation of volatile compounds of gold or silver with the baser metals.

Second. To the violent action on the surface of the metal during the decomposition of the oxidizing agent, thereby causing minute particles of the molten metal to be sprayed from the surface.

Third. To the upward current of air and flame sweeping over the surface of the molten metal in the pot drawing into the flue the vaporized metal and the fine spray.

These vapors are carried by the strong draught of the wind furnace out of the chimney, where they partially fall, in a sort of fine rain, upon the roof of the Mint and neighboring buildings, and a larger portion is carried into free space and lost.

Attempts have been made to recover the metal thus dissipated by means of shelves and other devices arranged in the flue, with but partial success, and they have the practical disadvantage of tending to impair the draught in the wind furnace.

It was to overcome these difficulties that an apparatus was devised by the writer to prevent the metallic vapors and gases arising from the

melting-pot from escaping into the flue at all by drawing them off into a suitable condensing chamber.

The Chief Assayer of the Mint, after examining the drawings, laid the whole matter before the late Director of the Mint in Washington, who in turn instructed the writer to have an experimental apparatus constructed, and "after it is finished to have it thoroughly tested by careful trials under the direction of the Melter and Refiner."

In accordance with these instructions the apparatus was made and erected at one of the furnaces in the melting department, and the trial tests were commenced on February 5th, 1878, and continued as opportunity offered until they were suspended, owing to the unprecedented increase in the regular work consequent upon the passage of the Bland Silver bill.

The arrangement of the experiments having been entrusted to the writer, he prepared a schedule of the proposed work, which was approved by the officers directly interested. It was designed by the writer that these trial melts should also subserve a broader purpose of furnishing reliable data as to the relatively injurious effects upon refined silver of small but known percentages of such base metals as were supposed to impair its good qualities. It is this secondary portion of the work which is now submitted, albeit in an incomplete form, to the readers of the JOURNAL OF THE FRANKLIN INSTITUTE.

The schedule as far as completed includes the preparation and subsequent examination, analysis and refining, of alloys of silver with arsenic, antimony, bismuth and lead.

About one thousand (1000) ounces of silver was adopted as the normal weight of refined metal to each experimental melt.*

With respect to the success of the apparatus, the writer desires merely to refer by permission to the brief extracts from letters of the officers, who observed its operation, which accompanied his report made to the late Superintendent of the Mint. These will be found in the foot note.†

* Although the assay department long since adopted the French system of weights, viz., the gramme and its decimals, the troy ounce is still regarded as the unit or standard Mint weight, and is accordingly employed in these experiments.

† Professor Booth, the Melter and Refiner, in whose department the tests were made, after endorsing the accompanying report as expressing the results of the trials in their integrity, says, "In relation to the TRIAL OF APPARATUS, I remark that the principle underlying Mr. Outerbridge's process is sound, viz., to recover volatilized precious metals by drawing off the possible vapors above gold and silver in a crucible and

He also desires to say that the credit for the success which attended the tentative tests of the apparatus is largely due to the excellent suggestions in the mechanical details which were made by Mr. Samuel James, the Master Mechanic of the Mint, to whom was entrusted the construction of the machine, thereby materially improving the original design.

FIRST EXPERIMENT—SILVER ALLOYED WITH ARSENIC.

Although the metal arsenic has a great affinity for silver, it will not readily combine with it in an open crucible, owing to its extreme volatility. The following expedient was therefore resorted to, with success :

A bar of silver which assayed 999 thousandths fine and weighed 100.46 ozs. (troy) was first melted with 3 ozs. of metallic arsenic in a black lead pot, with a lid luted on with fire-clay, and bound tightly with a metal strap.

The fire was brought up gradually for two hours, then a good white heat for half an hour ; it was then allowed to slowly die out ; the crucible remaining in its place was agitated in order to bring fresh surfaces of the molten silver in contact with the confined vapors of arsenic. A lump of charcoal was put in the crucible to prevent oxidation of the arsenic. When the pot was cold the "king" of metal was broken out, cleaned and weighed. It turned the scale at 102.98 ozs., showing that 2.52 ozs. of arsenic had combined with the silver.

The exterior surface of the "king," as it is technically called, presented a light grey color. On breaking it open this light shade was observed to extend to a depth of about $\frac{1}{20}$ th of an inch ; the interior showed a darker grey color, indicating that the surface contained a smaller proportion of arsenic. In order to ascertain this a piece was assayed from the surface and another from the interior, with the following result :

wholly condensing them. I remark further that his mode of effecting the result is, I believe, new, simple, effective and inexpensive," etc.

Mr. Wm. E. DuBois, the Chief Assayer, after alluding at some length to the evils which the apparatus was designed to overcome, says : "These two points being kept in view by all concerned, it was interesting to observe the changes and modifications by which the system (as all systems are) was step by step improved and simplified, until it seems nearly complete. Certainly it is now in such a satisfactory shape as would warrant its introduction into the mints and assay offices and refineries generally ; for it is well known that the evil which it abates is not confined to this institution."

Surface,	975 fine.
Interior,	971 fine.

It is possible that the portion of the metal touching the sides of the pot remained hot somewhat longer than the centre, owing to the fact that the pot remained in the fire until the whole had cooled. The volatile arsenic may thus have been driven (or distilled) *in* to the central portion of the solidifying mass.

The broken surface of the metal presented a clearly crystalline structure, and, although by no means so ductile as fine silver, it was far more so than could have been anticipated. The metal hammered and rolled without splitting. The solution in nitric acid was perfectly clear like fine silver, and no trace of arsenic could be detected by the eye or smell. Two samples of the alloy were preserved for future comparisons; one was rolled into a ribbon, to show the malleability; the other broken, to show the fracture.

In the next operation, 952 ozs. silver, 999 fine, were melted in a No. 40 black lead crucible. When the fine silver was perfectly fluid, the king of silver-arsenic alloy weighing 102.29 ozs., was added to the mass; the metal was then stirred and a sample for reference extracted

The metal was finally toughened in the ordinary way, using nitre and sand. At the end of one hour and a half the flux was skimmed from the surface and the metal poured into large shoe moulds.

The sample taken from the mass after the "king" was thoroughly incorporated, assayed 995 $\frac{1}{4}$, which agreed closely with the theoretical fineness, viz., 996. This sample was reserved for future experiments.

The mass metal, after having been toughened as above stated, was cast into bars, and assayed 998. The metal was then perfectly ductile, and no trace of arsenic could be detected by the eye.

The sweep resulting from the grinding of the crucible weighed 28 $\frac{1}{2}$ lbs. avoirdupois, and contained 97.712 grs. of pure silver per pound avoirdupois. The sweep from the grinding of the ashes in the furnace weighed 58 lbs., and contained .720 of a grain per lb. The entire weight of silver in both sweeps was thus found to be 1.12 oz. troy.

SECOND EXPERIMENT—WITH ANTIMONY.

The toughened silver resulting from the previous experiment was manipulated in the following way:

One bar, 998 fine, weighing 119.60 ozs., was melted in a closed

crucible with 3 ozs. of metallic antimony, with the addition of charcoal to prevent oxidation. The pot was allowed to cool slowly (as in the previous experiment with arsenic), and the king of alloyed metal resulting was found to weigh 122.39 ozs., showing that 2.79 ozs. of antimony had combined with the silver. The king assayed 975 fine, and contained $2\frac{1}{2}$ per cent. of antimony.

The metal was remarkably tough and ductile, rolling almost as well as fine silver; fracture crystalline and coarse.

Next a melt of silver bars, 998 fine, weighing 786.08 ozs. (resulting from the silver-arsenic experiment), was melted in a No. 40 black lead pot, under charcoal. As soon as it was fluid the king of antimonio-silver alloy was added. The whole was thoroughly stirred and a sample cast out for future experiments. This sample assayed 994 fine.

The metal was now exposed to a hot fire for a period of one hour and a half, a current of air being allowed to pass over the surface. Nitre was added occasionally in small quantities for the purpose of burning off the charcoal. During the entire time, the antimonio-oxyd was seen rising to the surface of the metal, and burning off with quite copious fumes, passing up the condensing tube. The water in the glass condensing chamber became very turbid, and the filter soon clogged up with a heavy sediment. The toughened metal was then cast into bars, and assayed 998 fine, and presented all the characteristics of fine silver.

The material on the filter was dried and collected. It weighed 1.15 ozs. An examination under the microscope showed that it was profusely sprinkled with extremely minute globules of metallic silver. These particles are nearly perfectly spherical, conclusively proving that they have been volatilized and condensed. The majority of the globules were very much smaller than the interstices of the filtering cloth, thus leading to the inference that a portion of the silver may have passed through the wash water, and thus escaped into the well. This fact was conclusively proved in the next experiment by collecting some of the water percolating through the filter, allowing it to settle, and recovering a button of pure silver from the sediment.

An analysis of the material showed that it contained one-seventh ($\frac{1}{7}$) silver, the remainder being antimonio-oxyd, colored by charcoal dust. The filter was burnt, and added to the precipitate; the metal was reduced to a button and cupelled. It weighed $\frac{13}{100}$ ounce.

THIRD EXPERIMENT—WITH BISMUTH.

One bar of toughened silver (resulting from previous experiment) assaying 998, weighing 137.77 ozs. was melted in a closed (luted) crucible with 3 ounces of bismuth in the same manner as before. The king of alloyed metal weighed 140.73 ozs., showing that 2.96 ozs. of bismuth had combined with the silver. The king resembled exteriorly the antimonio-silver alloy, but on cutting into the metal, it was found (unlike the antimonio-silver) to be exceedingly brittle or "short" like pie-crust. The fracture presented a coarse grain with a lustreless or earthy surface. The color of the metal when hammered was very dark or leady, and the strips had a somewhat greasy feeling.

The sample assayed 975 fine, showing about $2\frac{1}{2}$ per cent. of bismuth. A melt of 888.62 ozs. toughened silver, 998 fine, was then made in a No. 40 pot; as soon as it was melted the king was added. It was thoroughly incorporated with the mass by stirring; a sample was taken out and assayed 996 fine. The sample still showed plainly the "shortening" effect of bismuth; the fracture was crystalline and fine, the color was but slightly impaired and the assay slip rolled tolerably well.

The mass was now exposed to a high temperature for about three-quarters of an hour. Nitre was then added copiously, finally a small quantity of sand to thicken the flux just sufficiently to skim. The bars were cast into moulds, cleaned and weighed. On assaying the first and last bars it was found that but little or no improvement in fineness had occurred. The first bar assayed 996, the last $996\frac{1}{2}$; they were consequently reported $996\frac{1}{4}$.

The difficulty was, according to Professor Booth, that the nitre being thin, failed to hold the oxyd of bismuth formed by its action. As soon as the oxygen (formed by the decomposition of the nitre) had been driven off, the reducing action of the black-lead pot caused the bismuth to go back to the metallic state, when it again formed an alloy with the metal. (This metal was afterwards refined to $999\frac{1}{2}$ by the use of bone ash.)

As the examination of the precipitate collected on the filter in the previous experiment had revealed the fact that the volatilized silver globules were so minute as to lead to the inference that a portion had passed through the interstices of the filtering cloth, an effort was made to recover any particles thus escaping. The fact that the metal did so escape was conclusively proved in this experiment and a portion of the

fugitive particles recovered. In this case, the water percolating through the filter was caught in a large iron tank, the overflow from this tank discharged into a second filter composed of two thicknesses of fine twilled linen. The water in the tank was allowed to remain at rest for several hours and then drawn off. On testing the sediment in the tank, it was found to be rich in silver; it was then dried, treated with carbonate of soda in a sand-pot. A button of silver was obtained which was purified by cupellation and then weighed .07 of an ounce.

The sediment collected on the second filter was treated as above with a similar result. Finally a portion of the water escaping through the second filter was collected and silver was traced here also.

Although many of these particles or globules are so minute that a microscope with a good magnifying power is required to see them, they may be readily and beautifully exhibited by agitating a beaker-glass full of the water in the sunlight, when thousands of brilliantly scintillating points of light are seen reflected from the extremely minute faces of the silver pellicles. A similar effect is described by Faraday in "Philosophical Transactions," 1857. By treating very dilute solutions of gold with phosphorus he obtained the metal diffused through the liquid in extremely fine particles. These particles he says "are easily rendered evident by gathering the rays of the sun (or a lamp) into a cone by a lens, and sending the part of the cone near the focus into the fluid; the cone becomes visible, and though the illuminated particles cannot be distinguished, because of their minuteness, yet the light they reflect is golden in character and seen to be abundant in proportion to the quantity of gold present." He further says that portions of gold, in such a fine state of division that "they have not as yet been seen by any power of the microscope, may have the presence of the diffused solid particles rendered evident by the sun in this way."

SUPPLEMENTAL EXPERIMENT WITH THE SILVER BISMUTH ALLOY.

As already stated, the alloyed metal resulting from the experiment with bismuth was found to retain four and a half thousandths of bismuth which the nitre had not removed. In accordance with the suggestion of Professor Booth, the metal was again melted and covered with a coating of bone ash, holes were made in this covering with an iron poker and grains of nitre were dropped through to the exposed surface of the molten metal; as fast as the bismuth was oxidized it

was absorbed and held by the bone ash (the principle being the same as in cupellation); at the end of about one hour, the bone ash was taken off, a fresh supply of nitre and sand added, the second flux skimmed off and the metal cast into bars. The condensing apparatus was not used, as it was supposed that the bone ash covering would protect the metal from volatilization. It was found, however, that a loss of 1.42 ozs. occurred. During the toughening, samples were taken out at intervals of twenty minutes and assayed; the first showed 997 the metal still remaining brittle. The second sample assayed 997 $\frac{3}{4}$ and was also brittle. The third assayed 999 and showed some brittleness, but the fracture presented a closer grain than in the two former samples. It was still quite unfit for coin ingot metal.

The bars when cast had all the appearance of fine silver, being perfectly ductile; they assayed 999 $\frac{1}{2}$ fine. This result seems to indicate that small percentages of bismuth affect silver more injuriously, both in regard to its ductility and in respect to the difficulty of its elimination, than equal proportions of arsenic or antimony.

FIFTH EXPERIMENT—SILVER AND LEAD.

A bar of silver, 999 $\frac{1}{2}$ fine, weighing 82.83 ozs., was melted under charcoal with 3 ozs. of pure lead in a closed crucible. The king of alloyed metal weighed 85.61 ozs., showing that 2.78 ozs. of lead had combined with the silver.

The exterior of the king had a white or frosted appearance. On cutting an assay chip, the metal was found to be very brittle, having a dull leaden color. The fracture was not very clearly crystalline, but seemed more like the effect of a mechanical tearing away of the metal. A similar effect was noticed in rolling and hammering the assay slip, for while it broke to pieces under the hammer, it seemed to be crumbly (like dry bread) rather than brittle. Under ordinary inspection, however, it would have been simply classed as brittle. The sample from the king assayed 960, or contained 4 per cent. of lead. A melt of bars, 999 $\frac{1}{2}$ fine, weighing 931.53, was then made in a No. 40 black-lead pot. The king was added, mixed, and a sample cast; this sample assayed 996 $\frac{1}{4}$. It was fairly ductile, had a good lustre and color, but when compared with a strip of fine silver it was appreciably (though not greatly) darker in tint.

A coating of bone ash was put on and the nitreing performed as in the previous case. Samples were taken out and assayed from time to

time until the metal was found to be sufficiently refined. In about one hour the bone ash was removed and the bars cast. Owing to some accidental cause (probably the want of a sufficient covering of charcoal), the metal "spurted" or "vegetated" on the surface, rendering it necessary to remelt and recast the bars, and when this was done they presented to the eye all the characteristics of perfectly pure metal. When the small chip was cut off for assay, there was no evidence of a tendency to crystallization, and the sample was laminated into a ribbon $\frac{1}{100}$ th of an inch in thickness, without splitting. The assay showed that the metal was now refined to $999\frac{1}{2}$ thousandths.

To briefly recapitulate, the results obtained in this work—which the writer desires shall be regarded rather as preliminary, and therefore capable of possible modification on more extended investigation—are these:

It was ascertained that the arsenical silver alloy, contrary to the general expectation, was the least volatilizing in silver in comparison with more refractory metals, and that the alloy might contain one per cent. of arsenic (silver 990, arsenic 10) without materially injuring the ductility; but if carried to two and a half per cent., the mixture was quite brittle.

The antimonical-silver alloy caused a very much greater loss of silver, and yet its brittling effect was much less than had been anticipated. Bismuth was the most brittling, and in this experiment proved by far the most difficult to remove by fluxes that operated effectively upon the two former.

Lead caused a greater loss than any of the former with the exception of antimony. The brittleness of those was crystalline, of this rather crumbly or amorphous, yet three parts in a thousand did not spoil the ductility.

While it has been a source of regret to the writer that these trials have been suspended, for the reason given, prior to the completion of the pre-arranged schedule, he is led to hope that they may form the entering wedge into future investigations, which are much needed to afford a complete elucidation of the difficulties that beset the manipulator in the precious metals, whether in the preparation of coin metal, ornamental ware or gold leaf, in the want of ductility of the alloys, and he is also encouraged to think that they may serve to throw a passing glimmer of light upon this rather obscure subject, in support

of which hope he refers the reader to an extract on this subject from the letter of the assayer, already alluded to.*

TABLES.

The following tabular statement shows the gross weight of metal operated upon in each experiment and the amount of fine silver contained therein, together with the gross weight and amount of fine silver recovered from the toughening process :

FIRST EXPERIMENT.		OUNCES.	
		Gross Weight.	Fine Silver.
Refined silver, 999 fine,	.	1052·46	
Metallic arsenic,	.	2·52	
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Total weight of metal operated on,	.	1054·98	1051·40
Total weight of metal recovered in the form of bars, samples and "sweep,"	.	1053·32	1051·15
			<hr/>
Apparent loss of silver,	.		·25
SECOND EXPERIMENT.			
Refined silver, 998 fine,	.	905·68	
Metallic antimony,	.	2·79	
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Total weight of metal operated on,	.	908·47	903·86
Total weight of metal recovered,	.	903·16	900·21
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Apparent loss of silver,	.		3·65

* "I took a particular interest in this investigation for two reasons: First, I was sure that we knew too little practically about the effect of a small presence of such metals as arsenic, lead, etc. That is, we depended too much upon supposition, as to the extent or the degree in which they were injurious to the precious metals for coining purposes. It was worth while to make some severe and decisive tests upon that point. * * * As you have already seen by Mr. Outerbridge's report in detail, the alloying and volatilizing experiments were made with four metals in conjunction with silver, namely: arsenic, antimony, bismuth and lead. These are the chief enemies that trouble the camp of the silver miner and refiner. Nor are they less dreaded at the mint, since a small proportion of either will make our gold or silver refractory, brittle, crystalline or crumbly. * * * We must have ductile metal to work with. Hence these experiments have for us, as I have said, a twofold interest, as hitherto there have been no trials that we know of, at home or abroad, on any considerable scale, or in proper bulk. * * * On the whole we have learned a good deal, and I hope these experiments, without respect to the saving from waste, may be made accessible to parties interested in our own land and in foreign parts"

THIRD EXPERIMENT.

Refined silver, 998 fine,	1026·39	
Metallic bismuth,	2·96	
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Total weight of metal operated on,	1029·35	1024·33
Total weight of metal recovered,	1027·18	1023·31
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Apparent loss of silver,		1·02

FOURTH EXPERIMENT—(*Supplemental*).

Silver-bismuth alloy, 996½ fine,	1020·56	1016·73
Total weight of metal recovered,	1015·79	1015·31
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Apparent loss of silver,		1·42

FIFTH EXPERIMENT.

Refined silver, 999½ fine,	1014·36	
Metallic lead,	2·78	
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Total weight of metal operated on,	1017·14	1013·85
Total weight of metal recovered,	1011·78	1010·78
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Apparent loss of silver,		3·07

REMARKS ON THE GENERAL THEORY OF THE CENTRIFUGAL GOVERNOR FOR STEAM ENGINES.

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In any centrifugal governor, the masses moved by the centrifugal force resist the rotation by the inertia with a force equal to the masses multiplied by the acceleration. This force acting tangentially, it occasions a certain friction which resists the radial movement of said masses by the centrifugal force, which friction must be taken in consideration in the equation of dynamical equilibrium of the system.

If we indicate by ΣW , the sum of the weights moved by the centrifugal force in any centrifugal governor; by ρ , the variable distance of their common centre of gravity from the axis of rotation (the weights ΣW are supposed to have the same point of suspension); by