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TARNISH RESISTING SILVER ALLOYS

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REPORT OF A JOINT INVESTIGATION CONDUCTED BY THE BUREAU OF MINES AND THE BUREAU OF STANDARDS AT THE DIRECTION OF THE UNITED STATES SENATE COMMISSION ON GOLD AND SILVER INQUIRY

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TARNISH RESISTING SILVER ALLOYS

By Louis Jordan, L. H. Grenell, and H. K. Herschman

ABSTRACT

As one phase of the technical research on the uses of silver, undertaken at the direction of the United States Senate Commission on Gold and Silver Inquiry, the Bureau of Mines and the Bureau of Standards have determined some of the physical and mechanical properties of a wide variety of silver alloys, and have made a study of their resistance to tarnish in accelerated laboratory tests.

In this investigation were prepared and tested alloys of silver with aluminum, cadmium, copper, magnesium, zinc, silicon, tin, bismuth, antimony, tellurium, manganese, nickel, molybdenum, titanium, chromium, germanium, beryllium, gold, and sodium, chiefly in binary alloys and to a lesser extent in ternary and quaternary alloys.

For most of the alloys prepared determinations were made of the freezing point, density, tensile strength, and elongation of rolled and annealed sheets, and of the hardness of both the cast and the rolled and annealed alloys. Their comparative resistance to tarnishing was studied by exposure to a mixture of hydrogen sulphide and sulphur dioxide and by dipping in a sodium polysulphide solution.

Alloys of silver with cadmium or zinc were the most tarnish resistant of the workable binary alloys, but were also of the lowest tensile strength. Antimony and tin, either singly or together, were rather effective in strengthening zinc-silver alloys. These alloys also were readily workable and of marked tarnish resistance. Alloys of silver with 15 or 20 per cent of zinc or cadmium and 20 per cent of gold were very easily worked, possessed strength and hardness values more nearly comparable to copper-silver of sterling fineness than any of the other alloys prepared, and at the same time were very tarnish resistant.

None of the alloys made and tested in this investigation can be described as "nontarnishing." All could be tarnished under sufficiently severe conditions. Many of them, however, were distinctly more resistant to laboratory sulphur-tarnish tests than ordinary sterling silver.

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I. INTRODUCTION

Early in 1923 there was created by a resolution of the United States Senate the Senate Commission of Gold and Silver Inquiry. Among the duties of this commission was the investigation of the causes of the continuing decrease in the production of gold and silver, the causes of the depressed condition of the gold and silver industry, and the production, sale, and uses of gold and silver. Silver producers at that time were apprehensive of the future of the silver market, particularly at such time as the purchase of silver by the United States Treasury under the Pittman Act should cease.

Following the formation of the Senate commission, and at the direction of the Secretary of the Interior, the Bureau of Mines made a preliminary survey to determine in what way, if any, it appeared possible to increase the uses of silver. A report of this survey was made to the Senate commission. The commission then expressed the opinion that technical research on silver promised to be of great value and that such work by the Government was fully justified. Several lines of investigation were initiated, and the first report issued dealt with an investigation by the Bureau of Mines of the use of silver in detonators.[1]

The preliminary survey by the Bureau of Mines had indicated that one of the promising possibilities of any attempts to increase the use of silver would be the development of a silver alloy which should be nontarnishing, or at least less tarnishing than the usual sterling silver (copper-silver).

Some work had already been carried out at the Bureau of Standards on methods of testing silver alloys for their resistance to tarnishing, and a few tests had been made in cooperation with sterling silver manufacturers on special tarnish-resistant alloys. The proposed investigation looking toward the possible development of new tarnish-resisting silver alloys was, therefore, undertaken as a cooperative investigation by the Bureau of Mines and the Bureau of Standards. The present paper is the report on that joint research.

II. QUALITIES DESIRED IN A TARNISH-RESISTING SILVER

The opinion of the silver trade as to the possibilities of the commercial development of a tarnish-resisting silver is divided. Some manufacturers believe that the beauty of decorated silverware would be very largely lost if a silver alloy were used which was truly nontarnishing and did not darken by tarnish in the recessed portions of

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[1] C. A. Taylor and W. H. Rinkenbach, "Silver azide: An initiator of detonation," Army Ordnance, 5, pp. 824–825; 1925.

the design and thus give contrast with the high lights of the pattern. The opinion of the majority, however, seems to be that a really nontarnishing alloy of sterling quality would be a commercial possibility if it also possessed the same color as copper sterling and an equal degree of hardness and workability. They do not regard with favor an alloy which is only tarnish resisting; that is, one which tarnishes less rapidly than sterling but does ultimately blacken, since it is feared that the purchasers of such a silver, even though it were called "tarnish resisting" as distinguished from "nontarnishing," would expect to secure a nontarnishing material and dissatisfaction would result when the alloy finally did tarnish. Many silversmiths see but little promise, except for special applications, in an alloy which is not of sterling fineness since, due to effective advertising, the public has a very high regard for the sterling mark.[2]

Another consideration very important to silver manufacturers is the behavior of any alloy on remelting. Copper sterling silver scrap melts down cleanly, with very little change in composition. Any new silver alloy more liable to oxidation of one of its constituents on remelting would increase the difficulty of control of the fineness of the alloy and increase the costs of production.

Such considerations as the control of fineness of a silver alloy in large-scale preparation or in the remelting of scrap, the working qualities of the alloy in rolling, spinning, and decorating, and the distinguishing of slight differences in color of the untarnished alloys are all factors which can be determined most satisfactorily under plant conditions and by the manufacturers or fabricators of silverware. The present investigation is concerned chiefly with the laboratory preparation of silver alloys, accelerated laboratory tests of their tarnish resistance, and the determination of their mechanical properties. Some information on the workability of the alloys prepared is, of course, furnished by the data from the mechanical tests.

The laboratory tarnish tests of the present investigation were limited to tarnish by sulphur in one form or another. Such a limitation is justifiable in the case of silver alloys, since the tarnish which is objectionable to the users of silverware is that which blackens the metal, tarnish such as results from contact of silver with eggs or rubber, or the exposure of silver to sulphur-bearing gases from burning coal, oil, or gas.

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[2] The composition of silver alloys is generally expressed in the trade in terms of "fineness," and "sterling" silver is defined by law in the same terms. The fineness of a silver alloy is parts by weight of silver in 1,000 parts of the alloy. Sterling silver is "925 fine." Sterling silver, therefore, is at least 92.5 per cent silver with up to 7.5 per cent of alloying metal or metals.

III. PREVIOUS WORK ON TARNISH-RESISTING SILVER ALLOYS

1. DEVELOPMENT OF ALLOYS

The use of alloys of silver which should be less liable to tarnishing than copper-silver alloys was considered by Peligot in 1864.[3] Peligot made alloys of silver with 5, 10, and 20 per cent of zinc and noted that they all blackened less readily on exposure to hydrogen sulphide than the copper-silver coinage alloy. He also observed that the 20 per cent zinc alloy was more resistant to tarnish than the 5 per cent zinc alloy and stated that the 20 per cent alloy preserved its white color and polish even in solutions of polysulphides in which both coin silver and pure silver blackened rapidly.

Alloying palladium with silver as a means of decreasing tarnishing and the use of such alloys for graduated scales of mathematical instruments has also been reported.[4]

In 1895 Fowler and Hartog endeavored to develop a nontarnishing silver alloy which should also be capable of electrodeposition.[5] They report the preparation of alloys of silver with zinc, nickel, aluminum, and tin. They state that all of these alloys tarnish more easily than pure silver. Reference was made by Fowler and Hartog, and also by others in the discussion of their paper, to a company organized for the electrodeposition of silver-cadmium alloys which were claimed to be much less tarnishable than the usual silver alloy.

Escard[6] has stated that alloys of silver and aluminum are almost untarnishable, a statement, however, not in agreement with Fowler and Hartog.

Interest in tarnish-resisting silver alloys was revived in 1923 by the announcement from England that a new tarnish-resisting silver alloy named "Silanca," had been developed. The alloy was of sterling quality. Its composition has varied somewhat, but it appears to be an alloy of about 93 per cent silver with approximately 4.5 per cent antimony and either cadmium or zinc, or both, to make up the remaining 2.5 per cent.

American sterling silver producers and silversmiths have also done a very considerable amount of work in recent years on the development and testing of tarnish-resisting silver alloys. The results of this work were generously made available to the Bureau of Mines and Bureau of Standards, both in the initiation and planning and also throughout the progress of the present investigation.

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[3] E. Peligot, "Sur les alliages d'argent et de zinc," Ann. Chemie et Physique, No. 2, p. 430; 1864.

[4] Ure's Dictionary of Arts, Manufactures, and Mines, 7th edition, p. 96; 1878.

[5] G. J. Fowler and P. J. Hartog, "Notes on certain silver alloys," J. Soc. Chem. Ind., **14**, pp. 243–245; 1895.

[6] J. Escard, "Alloys of aluminum with rare or special alloys," Metal Ind. (London), **13**, p. 273; 1918.

2. METHODS OF TESTING TARNISH RESISTANCE

Any investigation attempting to develop tarnish-resisting alloys obviously necessitates the use of some method for comparing the tarnish-resisting qualities of the various alloys.

Peligot did not describe in detail the methods he used for determining the tarnish resistance of his silver-zinc alloys, but implies that they were tested both by exposure to hydrogen sulphide and by dipping in alkaline polysulphide solutions.

Fowler and Hartog determined the tarnish resistance of their alloys by placing a couple of drops of ammonium sulphide on the burnished surfaces of the alloy and of pure silver at the same time, removing the sulphide drops at the same time after an interval of a minute or two, and comparing the depth of color of the two stains.

Vernon,[7] in testing the tarnish resistance of pure silver, regular sterling silver, and a special sterling silver, containing 5.75 per cent copper and 1.75 per cent cadmium, exposed samples having both dull and polished surfaces to the atmosphere of a domestic kitchen for periods of 7, 16, and 32 days. The exposed specimens were judged both on the basis of visible darkening of the alloy and also by measurement of the loss of reflectivity. Vernon's tests showed that very different results were obtained on polished surface and on dull surface specimens. Vernon concluded that, under the exposure conditions he used, copper alloyed with silver largely inhibited the tarnish of polished surfaces. This observation is contrary to the results of the types of tarnish tests used in the present investigation.

In the course of some work at the Bureau of Standards on the electrolytic method for detarnishing silver, Vinal and Schramm[8] found it necessary to establish a standard method for tarnishing silver. This same method served also for the comparison of the tarnish resistance of various alloys of silver. The tarnishing conditions which they selected as most satisfactory were exposure of the polished specimens to a moist mixture of hydrogen sulphide and sulphur dioxide gas. Exposure for 15 minutes to a mixture containing 1 per cent hydrogen sulphide and 5 per cent sulphur dioxide was found to be suitable for applying a standard tarnish to pure silver or sterling silver.

Vinal and Schramm also made some tarnishing tests by dipping specimens in a tenth-normal solution of sodium sulphide in which flowers of sulphur had been dissolved.

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[7] W. H. J. Vernon, "First (experimental) report to the atmospheric corrosion research committee (of the British Nonferrous Metals Association)." Faraday Society Transactions, **19**, pp. 882–886; 1923.

[8] G. W. Vinal and G. N. Schramm, "The tarnishing and detarnishing of silver," Metal Ind. (New York), **22**, pp. 15–17, 110–111, 151–152, 231–233; 1924.

Several other methods of tarnishing have been used in recent work done in commercial and plant laboratories, notably the hard-boiled egg test. In this test one end of the polished specimens is placed in the crushed yolks of thoroughly hard-boiled eggs. All the specimens to be compared are placed at the same time in the mixture of yolks and allowed to remain for the same length of time.

Allowing tarnish-test specimens to remain in contact with flowers of sulphur, or to be wrapped in rubber bands, are other methods of testing tarnish resistance which have had some use.

IV. PREPARATION OF ALLOYS

1. GENERAL

The choice of the alloy compositions to be prepared and tested in the present investigation was made according to the following general plan: First, a survey was made of the binary alloys of silver with nearly all of the metals which were to be expected to alloy readily, namely, aluminum, antimony, beryllium, bismuth, cadmium, copper, germanium, gold, magnesium, manganese, silicon, tellurium, tin, and zinc. The preparation of binary alloys was also attempted with a few metals reported to be soluble in silver with difficulty, if at all, namely, chromium, nickel, tantalum, titanium, and molybdenum.

Tarnish tests were then applied to rolled and annealed or in some instances cast specimens of these alloys and the mechanical properties of the rolled alloys in the annealed condition were determined. On the basis of those results it was possible to select those alloying metals which showed the greatest effect in reducing the tarnish of silver and also those which had the greatest strengthening effect on silver.

Following the work with binary alloys attention was turned to ternary alloys with two objects in view; first, to attempt to "pull in" by means of the best tarnish-resistant alloying elements some of the metals not soluble in silver alone; for example, chromium, molybdenum, nickel, tantalum; second, to attempt to improve the more tarnish-resistant binary alloys by the addition of some one of the metals which had most noticeably increased the strength of silver in the binary combinations. Toward the conclusion of the work some binary alloys containing gold were made for purposes which will later be explained.

2. MELTING PROCEDURE

The alloys were all prepared in the high-frequency induction furnace, and in nearly all cases were melted in Acheson graphite crucibles fitted with a graphite cover which skimmed the melt on pouring. This cover was also provided with an opening for the insertion of a thermocouple and its protection tube. The alloys were cast in graphite molds. The cast ingots were about 3 inches long by 1 inch wide by one-half inch thick and weighed approximately 300 g.

The silver used as the base of all alloys was mint silver containing over 99.9 per cent pure metal. The chief impurities were about 0.06 per cent copper and 0.01 per cent gold.

The crucible charges were weighed out on the basis of 300 g for each ingot. The silver was melted first and generally heated to a little over 1,000° C. Then the alloying metal was added and stirred in with a graphite rod. The surface of the molten metal was covered with small pieces of graphite and the cover kept on the crucible except during additions of alloying metals or during stirring. After the addition of the alloying metal the temperature was raised to well above the melting point of the alloy, the heating stopped, and the freezing point or range of the alloy determined by means of a chromel-alumel thermocouple and a portable potentiometer.

The alloy was then again melted and heated to 150° to 200° C. above the freezing point and poured into the graphite mold. The ingot was next cropped at the top and all surfaces milled to a depth sufficient to remove irregularities and surface inclusions of oxides. Those millings taken from the ingot after complete removal of surface oxide were used for the chemical analysis of the alloy.[9]

3. ROLLING OF INGOTS AND PREPARATION OF TEST SPECIMENS

The cast ingots, after they had been cropped and their surfaces milled as described, were rolled cold with 5 per cent reductions per pass, requiring usually from 40 to 50 passes to give the desired 0.064-inch thick sheet. These reductions were much less severe than is the practice in rolling sterling silver. In some cases the milled ingots were annealed before rolling.

During the rolling the scleroscope hardness of the sheets was determined after every five or six passes. In the case of many of the alloys the hardness during the early stages of rolling increased rapidly, then reached a constant value, and the rolling could be continued to completion without annealing. Partly rolled sheets were annealed when they began to show cracks at the edges while the hardness was still increasing or when the scleroscope hardness increased above 40. The annealing for all alloys which were successfully rolled was at 650° C. for 30 minutes. Some of the alloys pre-

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[9] Chemical analyses by J. A. Scherrer and C. L. Buck, of the division of chemistry.

pared but not rolled to sheets, as, for example, the 15, 20, and 25 per cent aluminum-silver alloys and the 10 per cent bismuth alloy, contained a eutectic fusible below 650° C. and obviously were not annealed at the temperature named.

Tensile test bars of the dimensions shown in Figure 1 were prepared from these sheets. Tensile specimens of the silver alloys containing gold, tested during the conclusion of the investigation, were of the second type, *B*, shown in Figure 1, with a wider reduced section and a longer gauge length. Tarnish specimens were also cut from the rolled sheets. These specimens were approximately 2 inches long by ½ inch wide.

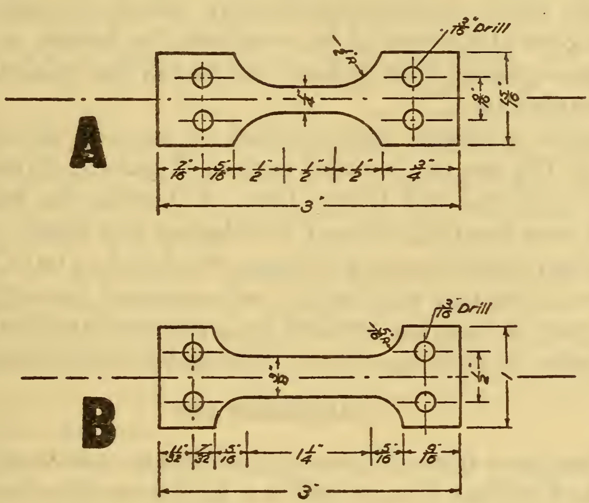

FIG. 1.—*Tensile test specimens*

A, specimen used for binary and ternary alloy series. *B*, specimen used for silver alloys containing gold.

V. TESTING OF ALLOYS

1. MECHANICAL AND PHYSICAL PROPERTIES

The scleroscope and Brinell hardness numbers (500 kg load, 10 mm ball) of the cast alloys were determined on the ingots after the surfaces had been milled. The hardness of the annealed sheets was measured with a "baby" Brinnell machine (12.8 kg load, 1.6 mm ball).

The ultimate strength and the elongation of the alloys as rolled to sheets and annealed were determined with an Amsler hydraulic testing machine on type A of the specimens described above for the binary and ternary silver alloys and with a Riehle machine on type B specimens for alloys containing gold.

The densities of all alloys were determined on the cleaned and polished tarnish-test specimens.[10]

2. TARNISH RESISTANCE

Tarnish-resistance tests were made on the 2-inch by ½-inch specimens cut from the sheets of such alloys as had been rolled. Specimens of approximately this same size were cut from cast ingots of those alloys which were not successfully rolled. In such cases the ingot was generally prepared by remelting the broken or imperfect bar or sheet resulting from the attempt to roll the original specimen of that composition.

The tarnish specimens were polished on one side on cloth buffing wheels with the use, in the order named, of pumice, tripoli, a white polishing compound, and Vienna lime. Following the polishing the specimens were carefully cleaned with benzol and finally with ether. This cleaning, following the polishing, was found to be of the utmost importance in securing satisfactory and consistent tarnish tests. Insufficient care in cleaning resulted in a streaked appearance of the specimen after tarnishing or in an abnormally dark tarnish film.

(a) GAS-TARNISH TEST

All alloys were tarnished both in moist air containing hydrogen sulphide and sulphur dioxide and in a tenth-normal sodium sulphide solution containing dissolved sulphur. The tarnishings in the gas mixture were carried out very nearly as described by Vinal and Schramm[11] and in the apparatus illustrated in their report. The "standard" tarnishing conditions used by Vinal and Schramm, namely, a 15-minute exposure in 1 per cent hydrogen sulphide and 5 per cent sulphur dioxide with moisture present, were found to be not severe enough to tarnish the more resistant alloys to a degree which would permit ready classification.

It was found most satisfactory both to lengthen the time of exposure of the specimens to 45 minutes and to increase the hydrogen sulphide in the gas mixture to 2 per cent. This more severe tarnishing test made evident the varying degrees of tarnish resistance of the more resistant alloys.

Repeated gas-tarnish tests on the same series or similar series of alloys made it clear that comparisons of the depth of tarnish of

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[10] Density determinations by Miss E. E. Hill, of the division of weights and measures.

[11] See footnote 8, p. 464.

specimens tarnished by this method at different times should be made only after due consideration of possible variables in tarnishing conditions. While the relative order of tarnish of the specimens of a series was found to be very nearly the same in different tests, the depth of tarnish of the series as a whole was found to vary appreciably. This variation seemed due to differences in the moisture content of the mixture of tarnishing gases. The tarnishing mixture of gases was made by evacuating a desiccator which contained the silver specimens suspended from glass hooks on a glass frame, and then introducing from a gas burette measured volumes of sulphur dioxide and hydrogen sulphide, both as dry gases. Air was then allowed to enter the desiccator to bring the pressure within up to atmospheric pressure. The moisture was introduced by allowing this air to bubble through a wash bottle containing water. This procedure obviously did not control with any exactness the proportion of moisture in the tarnishing gas mixture. The moisture content of the gas varied with the speed of the air flow and with the temperature of the air and water. Since it was not difficult to tarnish a large number of specimens at the same time and so secure satisfactory comparison of a great variety of alloys, and since precise control of the moisture would require that the entire tarnishing apparatus be kept at a constant temperature, no attempts were made to eliminate this variable.

Throughout the tarnish testing done in the present work no attempt was made to develop or employ any absolute measurement of the degree of tarnish of a specimen. As has been previously pointed out by Vinal and Schramm, the succession of colors on a silver specimen which has been progressively tarnished is rather definite, and may be taken as an indication of the degree of tarnish. Thus in the tabulated results of tarnishing tests of the alloys of this investigation the various alloy compositions have been grouped according to the "predominant tarnish color" of the specimens after a given test. These colors, in the order which represents the decreasing degree of tarnish, are "black, purple, brown, yellow, negligible."

In nearly all groups of alloys subjected to tarnish tests one or more control specimens were included, either standard sterling silver, pure silver, or any other particular composition selected for comparison. When no more precise designation of the degree of tarnish than the "predominant tarnish color" is employed, and when like control specimens in different tarnish tests have the same predominant tarnish color, it is possible to compare with some degree of assurance specimens tarnished at different times.

(b) SODIUM POLYSULPHIDE TARNISH TEST

The sodium polysulphide solution for tarnish testing was prepared by adding a small amount of free sulphur to a tenth-normal sodium sulphide solution, either warming this solution for 5 or 10 minutes on a steam bath or merely shaking and allowing to stand over night and filtering off the excess sulphur. The lower ends of a suspended set of the polished tarnish test specimens were immersed in this solution for either 1, 4, or 8 minutes and then removed and quickly rinsed in water and dried. In some respects this test is more satisfactory than the gas-tarnish tests. It is a more easily reproducible test and the comparison is readily made between the tarnished portion of the specimen and that part of the specimen above the line to which the specimens were immersed. In the case of very tarnish-resistant alloys this test thus permits the recognition of a much fainter tarnish film than does the gas test, in which the entire surface of a specimen is quite uniformly tarnished.

VI. BINARY SILVER ALLOYS

1. PREPARATION AND PHYSICAL PROPERTIES

The general plan on undertaking this investigation was to make binary silver alloys with 5, 10, 15, 20, and 25 per cent of the alloying metal. This plan was carried out completely in only a few cases, since preliminary tests often showed little promise even with the lower proportions of alloying metal or indicated increasing difficulty in working alloys of lower fineness.

The data on the composition and physical properties of the binary alloys are assembled in Table 1.

TABLE 1.—*Composition and physical properties of binary silver alloys*

Alloy No.	Composition		Freezing point	Color of alloy (polished surface)	Density at 25° C.	Tensile strength of annealed sheets	Elongation in 0.5 inch	Hardness		
	Intended alloying metal, per cent	Silver found by analysis, per cent						Ingot as cast		Annealed sheet: "Baby" Brinell
								Scleroscope	Brinell	
			° *C.*		*g/cm*^{3}	*Lbs./in.*^{2}	*Per ct.*			
S1	(Pure Ag)	99.95	960	White	10.49	25,000	60	5.5	30	35
SS	7.5 Cu	92.1	895	Slight yellow	10.33	44,000	46	19.0	77	76
1S1	5 Al	94.7	820	Gray	9.28	41,000	70	12.0	60	62
1S2	10 Al	89.9	740	Blue gray	8.33	-----	-----	32.0	119	-----
1S3	15 Al	84.7	700	do	7.49	-----	-----	34.0	143	-----
1S4	20 Al	79.1	650	do	7.35	-----	-----	35.0	143	-----
1S5	25 Al	74.3	620	do	6.21	-----	-----	27.0	119	-----
2S1	5 Cd	94.9	940	White	10.44	25,000	53	5.5	31	34
2S2	10 Cd	90.0	930	do	10.39	27,000	60	9.0	36	43
2S3	15 Cd	87.4	915	do	10.35	29,500	76	7.0	34	38
2S4	20 Cd	81.7	890	Slight yellow	10.29	32,000	76	9.0	36	43
2S5	25 Cd	75.5	875	Yellow	10.21	31,000	75	11.0	37	35
3SA	2 Mg	98.6	880	White	9.99	25,000	48	6.0	31	44
3S1	5 Mg	94.7	865	Light yellow	8.89	28,500	30	8.5	30	56
3S2	10 Mg	89.9	770	Light bronze	7.64	63,500	46	33.0	107	123
3S3	15 Mg	88.1	835	do	6.72	-----	-----	35.0	124	-----
4SA	3.5 Zn	95.5	930	White	10.34	25,000	54	2.5	31	46
4S1	5 Zn	94.3	910	do	10.27	27,500	80	7.0	34	36
4SC	7.5 Zn	92.2	890	do	10.20	31,500	74	4.0	33	51
4S2	10 Zn	89.7	880	Slight yellow	10.08	30,500	77	8.0	36	38
4S3	15 Zn	84.9	840	Light yellow	9.88	35,000	72	9.0	39	43
4S4	20 Zn	79.9	780	do	9.69	[1] 31,000	70	9.5	40	37
4S5	25 Zn	74.6	730	do	9.52	36,500	67	10.5	53	50
4SD	40 Zn	60.9	700	Pink	-----	-----	-----	30.0	124	-----
5S1	5 Si	94.9	940	Gray	8.93	-----	-----	16.0	74	-----
5S2	10 Si	89.7	1,115	Dark gray	8.14	-----	-----	17.0	93	-----
6S1	5 Sn	94.7	940	White	10.38	32,000	73	12.0	40	38
6S2	10 Sn	90.3	880	do	10.30	38,500	65	16.0	57	61
6S3	15 Sn	84.8	825	Dark silver	10.16	-----	-----	29.0	80	-----
7SA	1 Bi	98.3	950	White	10.45	-----	-----	5.0	32	-----
7S2	10 Bi	89.6	890	do	-----	-----	-----	8.0	38	-----
8S1	5 Sb	94.8	905	do	10.33	36,400	78	10.0	49	45
8S3	15 Sb	84.7	755	Gray	10.03	-----	-----	36.0	109	-----
8S5	25 Sb	74.8	570	Dark gray	9.70	-----	-----	43.0	119	-----
9SA	2 Te	97.4	945	Gray	10.33	-----	-----	8.0	34	-----
9SB	4 Te	94.7	935	do	10.15	-----	-----	9.0	40	-----
10SA	2 Mn	97.5	960	White	10.30	25,500	44	5.0	32	51
10SB	4 Mn	95.3	960	do	10.10	28,000	45	6.0	38	54
11SA	2 Ni	98.1	(960)	do	10.47	30,000	46	5.0	33	59
14S1A	5 Ti	(0.3A1, 0.18 Ti)	-----	do	-----	-----	-----	-----	34	-----
14S1B	5 Ti	(0.2A1, 0.1 Ti)	-----	do	-----	-----	-----	-----	31	-----
Cr 1	-- Cr	(0.14 Cr)	-----	do	10.48	27,500	48	4.0	28	49
Cr 2	2 Cr	(0.77 Cr)	-----	do	10.45	28,500	41	5.0	34	53
Ge 1	2 Ge	(2.1 Ge) [2]	-----	Light gray	-----	-----	-----	-----	-----	-----
Ge 2	4 Ge	(4.3 Ge) [2]	-----	do	-----	-----	-----	-----	-----	-----
Ge 3	6 Ge	(6.1 Ge) [2]	-----	do	-----	-----	-----	-----	-----	-----
B 1	2.5 Be	97.8	-----	do	9.57	-----	-----	11.0	[3] 66	-----

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[1] Imperfect sheet and test bars.

[2] Composition given by Prof. T. R. Briggs, of Cornell University, who prepared and loaned these alloys for tarnish tests.

[3] "Baby" Brinell hardness.

(a) PURE SILVER AND STANDARD STERLING SILVER

Melts of pure silver, the mint silver used as the basis of all subsequent alloys, and of standard sterling silver (copper-silver) were first made in order to provide two compositions with which the properties of the special alloys might be compared. The determinations of melting point, density, tensile properties, and hardness were thus made on pure silver and sterling silver on the same size specimens and under the same conditions as to size of melt, method of casting, cold working, and annealing as were the subsequent determinations on the special alloy compositions.

(b) ALUMINUM-SILVER

Aluminum-silver alloys containing 5, 10, 15, 20, and 25 per cent aluminum were prepared. In melting these alloys it was necessary to stir the aluminum vigorously into the molten silver with a graphite rod. Otherwise the oxide film on the surface of the added pieces of aluminum entirely prevented alloying.

The equilibrium diagram for the system aluminum-silver has been given by Petrenko[12] and recently briefly discussed by Saeftel and Sachs.[13] Escard[14] also has discussed the constitution, the preparation, and the properties of silver-aluminum alloys. According to the data of Saeftel and Sachs the limit of the solid solution of aluminum in silver is between 5.2 and 5.7 per cent by weight of aluminum. Petrenko's data indicate a second range of solid solution between 7.7 and 11.3 per cent of aluminum, a solid solution between two compounds, Ag_3Al and Ag_2Al.

The first of the alloys of this series made in the present investigation, containing 5.3 per cent aluminum, should consist chiefly, if not entirely, of the solid solution of aluminum in silver, with possibly a very small amount of the compound Ag_3Al as a second constituent. This alloy had a tensile strength and hardness comparable with ordinary sterling (7.5 per cent copper) silver and a very much higher elongation. It was rolled to a satisfactory sheet with two annealings. The strengthening effect of aluminum on silver in this alloy was greater than was found for the addition of 5 per cent by weight of any other alloying element used in the binary series.

None of the other aluminum-silver alloys prepared could be rolled. In the cast condition they were all extremely hard. This behavior is not surprising in view of the probable constitution of the alloys

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[12] G. J. Petrenko, "Über Silber-Aluminium Legierungen," Zeit. anorg. Chem. **46**, p. 53; 1905.

[13] F. Saeftel and G. Sachs, "Untersuchungen an den silberreichen festen Lösungen der Systeme Ag-Mg, Ag-Al, Ag-Sb, Ag-Sn, Ag-Zn, Ag-Cd, und Ag-Mn." Zeit. Metallkunde, **17**, pp. 155–161, 258–264, 294–298; 1925.

[14] See footnote 6, p. 463.

on the basis of Petrenko's diagram, namely, a solid solution of two intermetallic compounds for the 10 per cent alloy, and an intermetallic compound with increasing amounts of a eutectic for the 15, 20, and 25 per cent aluminum alloys.

The polished surface of the 5 per cent aluminum alloy had a distinct gray color. The color of the alloys became blue-gray with increasing amounts of aluminum.

(c) CADMIUM-SILVER

As in the case of aluminum, all the binary alloys contemplated in the general plan of investigation were prepared with cadmium, namely, 5, 10, 15, 20, and 25 per cent. The preparation of these alloys presented several difficulties. Cadmium, like aluminum, has a lower density than silver. Furthermore, its boiling point is lower than the melting point of silver. It thus vaporizes rapidly when added to the crucible charge of molten silver. Melting the alloys in a covered graphite crucible eliminated, in large part, the oxidation of the cadmium vapor while the melt was in the furnace. However, when the alloy was poured into the open graphite ingot mold, the vaporizing cadmium oxidized very rapidly, producing a heavy coating of brown oxide, often in lumps of considerable size, which were embedded rather deeply in the ingot surface and caused imperfections in the rolled sheets. This difficulty was in large part avoided by directing the reducing flame of an air-gas blast lamp across the open top of the ingot mold just before casting and pouring the alloy directly through this flame. These alloys all had a marked tendency to yield porous ingots if they were poured at too high a temperature.

The equilibrium diagram of silver-cadmium alloys has been studied by Petrenko and Federow.[15] The mechanical properties of silver-cadmium alloys have been discussed by Saeftel and Sacks.[16] The equilibrium diagram indicates that all the cadmium-silver alloys prepared in the present investigation were solid solutions of cadmium in silver in the field which extends from 100 per cent silver to alloys containing between 30 and 40 per cent cadmium.

All of these alloys prepared rolled readily to sheets. In contrast with the 5 per cent aluminum alloy, the 5 per cent cadmium-silver alloy exhibited no greater tensile strength or hardness than pure silver. Indeed, the 25 per cent cadmium alloy did not approach sterling silver or the 5 per cent aluminum alloy in strength or hard-

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[15] G. J. Petrenko and A. S. Federow, "Zur Frage über die Verbindungen des Silber mit Cadmium." Zeit. anorg. Chem., **70**, p. 168; 1911; and **71**, p. 217; 1911.

[16] See footnote 13, p. 472.

ness. It has been stated that silver-cadmium alloys with even small proportions of cadmium have a distinct yellow color. This color became unmistakable in the 20 and 25 per cent cadmium alloys of this series.

(d) MAGNESIUM-SILVER

Alloys of silver containing 5, 10, and 15 per cent magnesium were originally prepared. None of these, however, rolled satisfactorily, although sheets and tensile specimens could be prepared from the 5 and 10 per cent alloys. An alloy containing less than 2 per cent magnesium was subsequently made. Some trouble was experienced from oxidation of magnesium in the melting of these alloys. No special procedure was required other than plunging magnesium additions below the surface of the molten silver.

The equilibrium diagram for magnesium-silver given by Schemtschuschny[17] would indicate that the alloys of approximately 2 and 5 per cent magnesium were solid solutions; that the 10 per cent alloy would be rather close to the composition of a eutectic between the solid solution and the compound MgAg; that the approximately 15 per cent alloy would be in the field of the solid solution of the intermetallic compound MgAg with silver. Saeftel and Sacks,[18] however, state that the eutectic between silver and the compound MgAg shown in Schemtschuschny's diagram does not exist and that there is no break in the solid solution by magnesium in silver up to the composition of the compound MgAg.

Of the four alloys made in the present investigation only that of approximately 2 per cent magnesium (98.6 per cent silver by analysis) could be rolled to a sheet with a good surface, and this alloy was the only one of the four which did not have a distinct yellow or bronze color on its polished surface.

The alloy containing 1.4 per cent magnesium showed no increase in tensile strength or hardness over pure silver and the 5 per cent alloy but a slight increase. The 10 per cent magnesium alloy, however, had the highest tensile strength and hardness of any of the binary alloys from which it was possible to prepare tensile specimens. Its values for tensile strength of 63,000 lbs./in.^{2}, with elongation of 46 per cent, and hardness of 33 scleroscope and 107 Brinell are to be compared with the corresponding values for the sterling silver test specimens of 44,000 lbs./in.^{2} tensile strength, 46 per cent elongation, and 19 scleroscope and 77 Brinell hardness. Guertler[19]

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[17] S. F. Schemtschuschny, "Über die Legierungen des Magnesium mit Silber." Zeit. anorg. Chem., **49**, p. 400; 1906.

[18] See footnote 13, p. 472.

[19] W. Guertler, "New alloys of silver," Metal Industry (London), **27**, p. 485; 1925.

has recently called attention to the very marked strengthening effect of suitable additions of magnesium to silver.

(e) ZINC-SILVER

Silver-zinc alloys containing 5, 10, 15, 20, and 25 per cent zinc were made initially and later additional alloys containing approximately 4.5, 7.5, and 40 per cent of zinc were prepared. The same precautions were taken to reduce oxidation of zinc during melting and pouring as in the case of the cadmium alloys.

The equilibrium diagram for this system has been given by Carpenter and Whiteley,[20] and Saeftel and Sacks[21] discuss the mechanical properties of silver-zinc alloys. The very close resemblance of the silver-zinc diagram to the silver-cadmium diagram has been pointed out by Guertler[22] and by Carpenter. All the silver-zinc alloys prepared in the present series up to and including that containing 25 per cent zinc were in the field of the α solid solution, were readily rolled to sheets, and showed only a moderate increase over pure silver in tensile strength and hardness, thus resembling the corresponding silver-cadmium alloys. The hardening effect of a given per cent by weight of zinc was slightly greater than for cadmium. A faint yellow color appeared in the 10 per cent zinc alloy and persisted through the 25 per cent composition. The 40 per cent zinc alloy, lying within the $\alpha+\gamma(Ag_2Zn_3)$ eutectoid range, was too brittle to permit rolling and was of a distinct pink color after a short time standing in the air.

The 7.5 per cent zinc alloy is to be particularly noted as being of sterling fineness, possessing good color, a melting point and density close to that of the copper-sterling alloy, of greater elongation but of appreciably lower tensile strength and lower hardness than the copper alloy.

(f) SILICON-SILVER

Two silver-silicon alloys were prepared, containing 5 and 10 per cent silicon, by the addition of suitable amounts of a 50 per cent silver-silicon alloy to molten silver.

The equilibrium diagram given for this system by Arrivant[23] shows a eutectic at approximately 4 per cent silicon and indicates no field of solid solution on the silver side of the diagram. Neither of the alloys prepared in the present investigation were workable in the cold. They both had a very distinct gray color.

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[20] H. C. H. Carpenter and W. Whiteley, "The silver-zinc equilibrium," Internat. Zeit. Metallog., **3**, p. 145; 1913.

[21] See footnote 13, p. 472.

[22] W. Guertler, Metallographie, **1**, p. 499; 1912.

[23] G. Arrivant, "Sur les alliages de silicium et d'argent," Compt. Rend., **147**, p. 859; 1908.

(g) TIN-SILVER

Silver and tin alloyed readily, and the cast ingots had very clean surfaces. Only the 5, 10, and 15 per cent alloys of this series were prepared.

Murphy[24] has recently published the diagram for this system, modifying the earlier one by Petrenko. According to Murphy's diagram, the 5 and 10 per cent alloys consist of the α solid solution. Both of these alloys rolled to sheets possessed a good white color and very appreciably greater strength and hardness than the alloys containing corresponding proportions, by weight, of cadmium or zinc. The alloy containing 15 per cent of tin was in the range shown in Murphy's diagram as the β solid solution. This alloy was not workable and was not as white as the alloys of lower tin content.

(h) BISMUTH-SILVER

Bismuth-silver alloys were easily prepared with a negligible amount of oxidation and were cast as sound ingots. Only the 1 and 10 per cent alloys were prepared, since it has been quite generally stated that a very small amount of bismuth in silver increases the brittleness of the metal to a point where cold-rolling is impossible. The data for the equilibrium diagram of this system by Petrenko[25] suggests a small, not definitely determined, solubility of bismuth in silver. The approximately 1 per cent (98.3 per cent silver by analysis) alloy was prepared as possibly within this range, and the 10 per cent alloy simply for tarnish tests in the cast condition as the very low melting eutectic (262° C.) in this composition would make the alloy hardly practicable for working and fabrication. Not even the approximately 1 per cent bismuth alloy could be rolled.

(i) ANTIMONY-SILVER

Alloys were made containing, respectively, 5, 10, and 15 per cent of antimony with silver.

On the basis of the diagram for silver-antimony by Petrenko,[26] the 5 per cent alloy is a homogeneous, solid solution, while the 10 and 15 per cent alloys consist of this solid solution, together with the compound Ag_3Sb. The strength and hardness of the 5 per cent alloy was greater than for the corresponding tin alloy but less than for the 5 per cent aluminum-silver composition. It had a satisfactory white color and was successfully rolled. The 10 per cent antimony

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[24] A. J. Murphy, "The constitution of the alloys of silver and tin," J. Inst. Metals, **35**, pp. 107–124; 1926.

[25] G. J. Petrenko, "Über die Legierungen Silbers mit Thallium, Wismut, und Antimon," Zeit. anorg. Chem., **50**, pp. 133–144; 1906.

[26] See footnote 25.

alloy was colored gray and could not be rolled. The 15 per cent alloy was a still darker gray. No attempt was made to roll this latter alloy.

(j) TELLURIUM-SILVER

Two alloys of silver and tellurium were made containing approximately 2.5 and 5 per cent tellurium. Both of these alloys possessed a distinct gray color. Neither of them could be cold rolled. According to the diagram of Pellini and Quercigh,[27] both alloys should be composed of pure silver with the silver-Ag_2Te_2 eutectic in smaller and larger amounts, respectively.

(k) MANGANESE-SILVER

Two alloys of silver with manganese were prepared, containing approximately 2.5 and 4 per cent manganese. Both alloys rolled to sheets rather readily, but showed little increase in strength over pure silver. Both of these alloys should be solid solutions according to the diagram of the silver-manganese system given by Arrivant.[28] The mechanical properties of silver manganese alloys have been studied by Saeftel and Sachs.[29]

(l) NICKEL-SILVER

A single alloy of nickel with silver was prepared containing 2 per cent nickel. This alloy was cast at a temperature of approximately 1,200° C., which should be in the field of a single liquid phase according to Petrenko.[30] Casting from this temperature with rapid freezing should result in the reasonably uniform distribution in the silver matrix of the solid solution of silver in nickel existing at the nickel side of the diagram. The alloy worked quite satisfactorily, and, for the small amount of alloying metal, showed a considerably greater hardness than pure silver.

(m) MOLYBDENUM-SILVER AND TANTALUM-SILVER

The attempts to alloy molybdenum and tantalum with silver by direct addition of the metallic elements to molten silver were unsuccessful.

(n) TITANIUM-SILVER

Two attempts were made to prepare a silver alloy containing 5 per cent of titanium, alloys 14S1A and 14S1B. The first alloy was

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[27] G. Pellini and E. Quercigh, "I telluri d'argento," Atti. R. Accad. Lincei, 19, ii, p. 415; 1910.

[28] G. Arrivant, "Die Legierungen von Mangan und Silber," Zeit. anorg. Chem., 83, p. 193; 1913.

[29] See footnote 13, p. 472.

[30] G. J. Petrenko, "Über die Legierungen des Silbers mit den Metallen der Eisengruppe." Zeit. anorg. Chem., 53, pp. 212–215; 1907.

melted in a graphite crucible and the second in a zirconia crucible. Very considerable formation of dross in each case prevented casting of the melts. The titanium was added as 85 per cent metallic titanium. No analysis of this material was available nor made after receipt. The analyses of the resulting ingots, however, indicate that the metallic titanium contained aluminum. Approximately 0.2 and 0.1 per cent of titanium was found in the final alloys. These alloys were rolled to sheets, but no tensile tests were made.

(o) CHROMIUM-SILVER

Two attempts were made to prepare chromium silver alloys. In the first case metallic chromium was added equivalent to 15 per cent chromium in the silver and the temperature of the melt raised to over 1,200° C. The analysis of the resulting metal indicated the presence of 0.14 per cent chromium. In the next attempt chromium equivalent to only 2 per cent was added, but the temperature of the melt was increased to approximately 1,500° C. The resulting ingot in this case contained 0.77 per cent chromium. Both of these ingots were rolled to sheets and showed some increase in strength and hardness over pure silver.

(p) GERMANIUM-SILVER

Alloys of germanium with silver were not prepared in this investigation, but three specimens containing approximately 2, 4, and 6 per cent germanium were kindly loaned by Prof. T. R. Briggs, of Cornell University. The small samples available did not permit the determination of mechanical properties. They were rolled only sufficiently to give flat surfaces for tarnish tests. All three germanium-silver alloys were of a light gray color.

(q) BERYLLIUM-SILVER

A single alloy was prepared of beryllium with silver. Although the small addition of metallic beryllium, to make a 2.5 per cent alloy, was held beneath the surface of the molten silver in preparing this alloy, there was so much formation of dross, apparently from oxidation of the beryllium, that it was not possible to pour the melt. The silver was hardened very considerably, but the alloy could not be rolled cold.

2. TARNISH RESISTANCE

The tarnish tests on the binary alloys were carried out, as already described, both by exposure to moist air containing hydrogen sulphide and sulphur dioxide and by dipping in 0.1 normal sodium sulphide containing an excess of sulphur. The results of the tarnish tests on all the binary alloys are given in Table 2. It is there shown that the original conditions used by Vinal and Schramm for gas-tarnish tests of silver, namely, 15 minutes in moist air containing 1 per cent hydrogen sulphide and 5 per cent sulphur dioxide, were not severe enough to indicate any considerable differences in a large group of the more tarnish-resistant alloys of the present series. Increasing the time of exposure with the same gas mixture decreased the number of alloys which showed a negligible tarnish color and doubling the concentration of the hydrogen sulphide in the mixture, still further separated the more tarnish-resistant specimens.

TABLE 2.—*Results of tarnish tests on binary alloys of silver*

Tarnish test No.	Conditions of tarnish test	Predominant tarnish color of specimens after test [1]				
		Black	Purple	Brown	Yellow	Negligible
1	15 minutes; 1 per cent H_2S, 5 per cent SO_2, moist air.	--------	7.5 Cu 4 Te	15; 10; 5 Mg Sp. No. 99 25 Al	2 Te 2 Mg 10; 5 Al 1 Bi 0.77 Cr Sp. No. 98 15 Sn 10; 5 Si	20; 15 Al Pure silver 0.14 Cr 25; 15; 5 Sb 10; 5 Sn 5; 10; 15; 20; 25 Cd 5; 10; 15; 20; 25 Zn
2	45 minutes; 1 per cent H_2S, 5 per cent SO_2, moist air.	15 Mg	4; 2 Te 7.5 Cu 20; 15; 10; 25 Al 10; 5 Mg 1 Bi 10; 5 Si	2 Mg 15 Sb 15 Sn	5 Al Pure silver 0.14; 0.77 Cr 5 Sb Sp. No. 98; 99 10; 5 Sn 5; 10 Cd	25 Sb 15; 20; 25 Cd 5; 10; 15; 20; 25 Zn
3	45 minutes; 2 per cent H_2S, 5 per cent SO_2, moist air.	15; 10 Mg 7.5 Cu 2; 4 Te	5; 2 Mg Sp. No. 99 10; 15; 5 Al Pure silver 5; 10 Si 1 Bi 15 Sn 5 Cd	0.14; 0.77 Cr 5 Sb 10; 5 Sn 10; 15 Cd 5; 10; 15 Zn	20; 25 Cd Sp. No. 98	15 Sb 20; 25 Zn
4	8 minutes; sodium polysulphide.	7.5 Cu 5 Al 2; 10; 15 Mg	10; 15; 20; 25 Al 2; 4 Te 2; 4 Mn 2 Ni 5; 10 Si Pure silver	5 Mg 1 Bi 0.14; 0.77 Cr 5 Sb 5 Cd	15; 25 Sb 5; 10; 15 Sn 3.5; 5 Zn 10; 15 Cd	20; 25 Cd 5.5; 7.5; 10; 15; 20; 25 Zn
5	1 minute; sodium polysulphide.	--------	7.5 Cu 6.1 Ge	4.3 Ge	2.1 Ge Pure silver 7.5 Zn 4.6 Zn, 2.7 Sb [2]	
12	8 minutes; sodium polysulphide.	7.5 Cu	0.1 Ti (0.2 Al) Pure silver 0.2 Ti (0.3 Al)	--------	4.6 Zn, 2.7 Sb [2]	

[1] Within each block of the table the alloys are arranged in the approximate order of decreasing tarnish.

[2] Ternary alloy included for direct comparison of tarnish resistance.

The specimens listed in Table 2 as Nos. 98 and 99 were samples of two tarnish-resisting silvers that have to some extent been developed commercially. They are ternary and quaternary alloys, respectively. Their compositions are given in Table 3 with the ternary alloys prepared in the present investigation. The tarnish tests of Table 2 show that the specimens containing certain of the alloying metals can be classed as, in general, more liable to tarnish than pure silver. Such alloys are those of silver with copper, aluminum, germanium, magnesium, manganese, tellurium, bismuth, and nickel. On the other hand, alloys containing antimony, tin, cadmium, and zinc were at least as resistant to tarnish as was pure silver.

The more severe tarnishing conditions of tests 2, 3, and 4 indicated that the alloys containing the higher proportions of cadmium and zinc were very appreciably more resistant to tarnish than pure silver and that the alloys with antimony and tin, as well as the compositions containing the lower percentages of cadmium and zinc were more heavily tarnished, but were still somewhat better than the pure silver comparison specimens.

The tarnish series listed in Table 2 under test No. 4 shows that the general order of tarnish of the binary alloys was very nearly the same after dipping in sodium polysulphide solution as after exposure to the tarnishing gas mixtures. The silver-manganese alloys and the silver-nickel specimen which were not included in gas-tarnish tests were included in this test. These were all somewhat more heavily tarnished than pure silver.

Tarnish test No. 5 was made at a later date than the other tests in Table 2 for the purpose of determining the tarnish resistance of the three silver-germanium alloys loaned by Professor Briggs, of Cornell University. The three germanium alloys were tested with control specimens of standard (copper) sterling silver, pure silver, a 7.5 per cent zinc alloy, and one of the more tarnish-resisting ternary alloys to be described below. The germanium alloys all proved to be more readily tarnished than pure silver.

Tarnish test No. 12 was made on the silver alloys containing small amounts of titanium (with aluminum). These alloys tarnished to about the same degree as pure silver.

The single binary alloy of beryllium with silver was available for tarnish tests only after the completion of the general tests of the binary alloys. The beryllium-silver specimen was included in the tarnish tests of silver alloys containing gold. These tests are given in Table 6 where it is evident that the beryllium-silver alloy in both the gas-tarnish test and the polysulphide-solution test is tarnished as much or more than the standard sterling silver control specimen.

3. SUMMARY OF PROPERTIES OF BINARY ALLOYS

The tarnish tests of the binary alloys, therefore, indicated that additions of zinc and cadmium to silver very appreciably decreased the liability of pure silver to tarnish in sulphur gases or in sodium polysulphide solution, and that progressively greater resistance to tarnish was secured by additions of either of these alloying metals in increasing amounts up to 25 per cent. Antimony and tin were also shown to increase the resistance of silver to tarnish, but not to quite so marked a degree as cadmium or zinc. Copper, germanium, beryllium, aluminum, magnesium, tellurium, and nickel appeared to increase the tarnishing of silver. Silicon, and the very small amounts of chromium and titanium which were introduced into silver had comparatively little influence either in increasing or decreasing tarnish formation. A typical set of tarnished binary alloy specimens is illustrated in Figure 2.

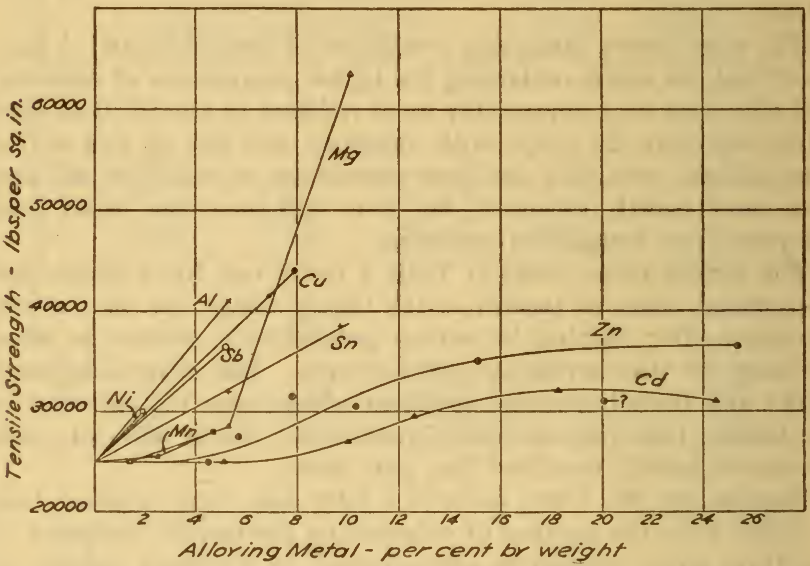

FIG. 3.—*Effect of alloying metals on the tensile strength of silver in binary alloys*

Cadmium and zinc, therefore, stand out as the most effective alloying metals in binary combinations with silver to reduce sulphide tarnish formation. Both the cadmium-silver and the zinc-silver alloys containing the higher proportions of base metal possess a yellowish color, which is somewhat more pronounced in the cadmium alloys than in the zinc alloys. Both of these series of alloys

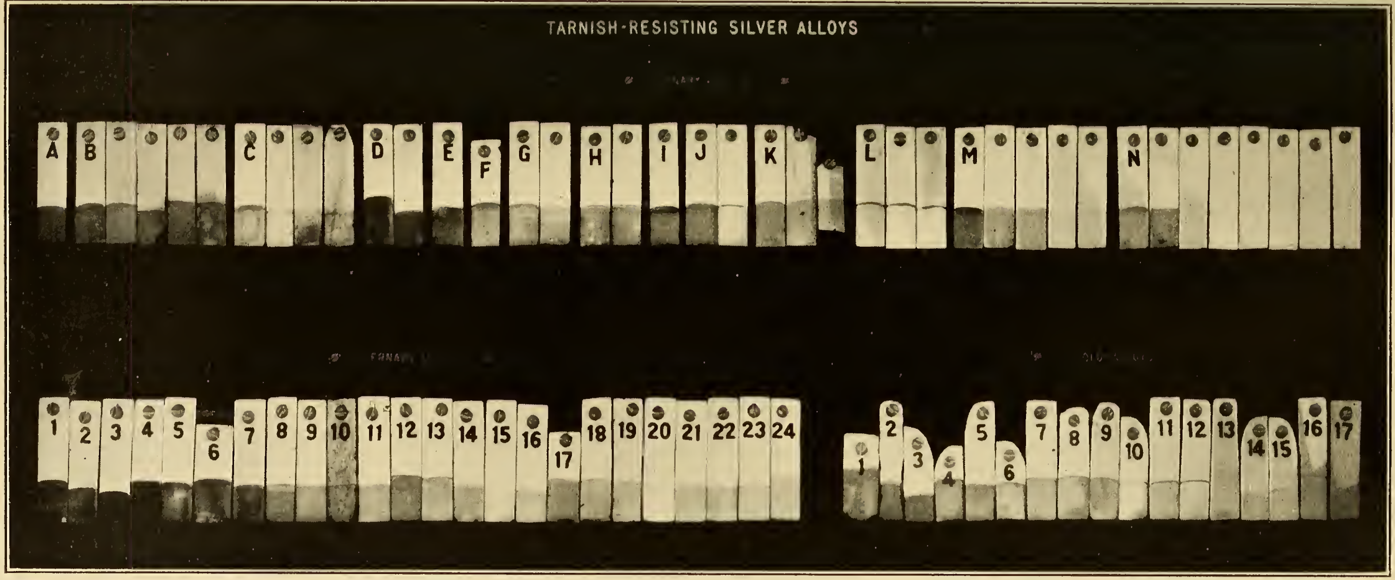

FIG. 2.—*Tarnished specimens of silver alloys*

Specimens tarnished for eight minutes in tenth normal sodium sulphide containing an excess of sulphur. Numbers following name of alloying metal indicate approximate parts per hundred of that metal in silver alloy

BINARY ALLOYS

A—Copper, 7.5 (usual sterling silver).
B—Aluminum, 5, 10, 15, 20, 25.
C—Magnesium, 2, 5, 10, 15.
D—Tellurium, 2, 4.
E—Nickel, 2.
F—Bismuth, 1.
G—Manganese, 2, 4.
H—Silicon, 5, 10.
I—Pure silver.
J—Chromium, 0.14, 0.77.
K—Antimony, 5, 15, 25.
L—Tin, 5, 10, 15.
M—Cadmium, 5, 10, 15, 20, 25.
N—Zinc, 3.5, 5, 5.5, 7.5, 10, 15, 20, 25.

TERNARY ALLOYS

1—Nickel 1.8, copper 2, tantalum 0.
2—Nickel 0.5, antimony 1.5, chromium 0.1.
3—Aluminum 0, tantalum 0.
4—Nickel 1, molybdenum 0.
5—Cadmium 5, nickel 0.5.
6—Copper 2.6, zinc 3.9.
7—Antimony 3.5, nickel 1.
8—Manganese 4, molybdenum 0.
9—Zinc 5, nickel 0.5.
10—Aluminum, molybdenum (no analysis).
11—Cadmium 5, chromium 0.06.
12—Antimony 3, tantalum 0.

TERNARY ALLOYS—Continued

13—Tin 6, nickel 1.
14—Zinc 4.5, antimony 2, tin 1.
15—Zinc 5, magnesium 2.
16—Zinc 5, tin 2.
17—Cadmium 3.4, antimony 3.2.
18—Antimony 5, chromium 1.
19—Zinc 5, aluminum 2, molybdenum 0.3.
20—Zinc 5, chromium 0.2.
21—Zinc 4.5, antimony 2, aluminum 1.
22—Zinc 5, aluminum 2.
23—Tin 5, chromium 1.
24—Antimony 2.5, zinc 4.5.

GOLD

1—Beryllium 2.2.
2—Beryllium 1.6, gold 6.
3—Gold 5, aluminum 2.
4—Gold 5, cadmium 2.
5—Gold 8.5, nickel 0.7.
6—Gold 7.5.
7—Gold 8, nickel 2.
8—Gold 7, chromium 0.3.
9—Gold 32.8, chromium 0.6.
10—Gold 5, antimony 2.
11—Gold 15, chromium 0.4.
12—Gold 20.
13—Gold 0.6, zinc 20.
14—Gold 21.5, cadmium 19.
15—Gold 20, zinc 14.
16—Gold 50.
17—Gold 75.

are very easily rolled to sheets, but have tensile strengths and hardness values but little higher than pure silver. The relative tensile strengths of the workable binary silver alloys are shown in Figure 3. This figure indicates that the alloy additions having the greatest strengthening effect on silver and at the same time producing alloys which can readily be cold-rolled are aluminum nickel, antimony, copper, and tin. The tarnish tests of the binary alloys showed that of these additions only antimony and tin acted also to decrease the tarnish formation on silver. Any further steps, therefore, aiming to increase the strength of the most tarnish-resistant binary alloys by the addition of a second alloying element to secure increased strength might well be the addition of antimony or tin to silver-cadmium or silver-zinc alloys.[31]

VII. TERNARY-SILVER ALLOYS

1. PREPARATION

As already stated, two objects were in view in making the ternary alloys—first, to attempt to alloy with silver in ternary combinations some of the metals which were not soluble in silver alone, and, second, to modify the mechanical properties, increase the strength and hardness, of some of the more tarnish-resistant binary alloys.

The first group of ternary alloys was prepared with this former purposes, namely, to attempt to alloy chromium, nickel, molybdenum, and tantalum with silver and some third metal known to alloy readily with silver alone. The compositions and the mechanical properties of the ternary alloys are listed in Table 3. In all cases the fineness of these alloys was intended to approximate that of sterling silver.

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[31] Compare the recently granted patent on a silver-cadmium-antimony tarnish-resisting alloy. Robert H. Leach, United States Patent No. 1628673, May 17, 1927.

TABLE 3.—*Composition and physical properties of ternary silver alloys*

Alloy No.	Composition		Freezing point	Color of alloy (polished surface)	Density at 25° C.	Tensile strength of annealed sheets	Elongation in 0.5 inch	Hardness		
	Intended alloying metals, per cent	Found by analysis, per cent						Ingot as cast		Annealed sheet: "Baby" Brinell
								Scleroscope	Brinell	
			° *C.*		*g/cm*^{3}	*Lbs./in.*^{2}	*Per cent*			
TS1	Sb 5, Cr 2	93.4 Ag, 5.3 Sb, 1.2 Cr	------	White	10.28	--------	------	7	42.9	------
TS2	Sn 5, Cr 2	93.7 Ag, 5.2 Sn, 1 Cr	------	do	10.35	35,500	70	6	36.2	51.5
TS3	Zn 5, Cr 2	95 Ag, 4.7 Zn, 0.2 Cr	------	do	10.27	30,500	66	5	31.2	44.5
TS4	Cd 5, Cr 2	95.2 Ag, 4.7 Cd, 0.06 Cr	------	do	10.42	28,500	43	4	31.2	57
TS5	Sb 5, Ni 2	95.4 Ag, 3.5 Sb, 1 Ni	960	do	10.40	--------	------	8	42.4	------
TS6	Sn 5, Ni 2	93.6 Ag, 5.6 Sn, 0.8 Ni	940	do	10.36	33,000	58	9	47.5	50.5
TS7	Zn 5, Ni 2	94.5 Ag, 4.7 Zn, 0.6 Ni	930	do	10.27	33,000	59	5	32.8	51
TS8	Cd 5, Ni 2	95.1 Ag, 4.5 Cd, 0.5 Ni	940	do	10.44	30,500	46	4	31.2	57
TS9	Sb 5, Mo 1.5	Did not alloy	------	----------	------	--------	------	-----	------	------
TS10	Al 5, Mo 2	No analysis	------	----------	------	--------	------	-----	------	------
TS11	Mn 5, Mo 2	95.7 Ag, 4 Mn, Trace Mo	960	Light gray	10.07	28,000	46	5	31.2	54
TS12	Ni 5, Mo 2	98.6 Ag, 1.3 Ni, 0 Mo	960	do	10.37	30,500	46	7	32.8	57
TS13	Zn 4.5, Sb 2.5	92.6 Ag, 4.6 Zn, 2.7 Sb	880	do	10.21	35,000	78	8	38.1	44.5
TS14	Zn 5, Al 1.5, Mo 0.5.	92.1 Ag, 2.1 Al, 5.3 Zn, 0.3 Mo	820	do	9.70	40,000	------	14	48.9	54
TS15	Zn 5, Al 2	93.1 Ag, 4.5 Zn, 2.3 Al	880	do	9.78	37,500	76	6	40.2	40
TS16	Zn 5, Sn 2	92.6 Ag, 5.2 Zn, 2 Sn	890	White	10.23	32,000	78	5	34.4	30
TS17	Zn 5, Te 2	92.8 Ag, 4.8 Zn, 2.1 Te	880	Gray	------	--------	------	8	40.2	------
TS18	Zn 5, Mg 2	92.7 Ag, 5.2 Zn, 1.9 Mg	870	White	9.62	35,500	65	7	41.3	44.5
TS19	Ni 5, Cr 2	97.6 Ag, 0.1 Cr, 0.6 Ni, 1.6 Sb	------	do	10.42	30,000	28	15	------	52.5
TS20	Sb 5, Ta 2	96.9 Ag, 3.1 Sb, 0 Ta	------	do	10.41	29,500	78	10	38.1	35.5
TS21	Al 5, Ta 2	99.2 Ag, 0 Ta, 0 Al	------	do	10.48	29,500	45	7	31.2	48
TS22	Si 4, Cd 3.5	92.6 Ag, 3.2 Si, 4.1 Cd	------	do	------	--------	------	16	144	------
TS23	Na 0.5, Zn 6.5	92.8 Ag, <0.1 Na, 7 Zn	------	do	------	--------	------	-----	35	------
QS1	Zn 4.5, Sb 2, Al 1.	92.6 Ag, 4.5 Zn, 2.1 Sb, 0.7 Al	870	do	9.65	33,000	76	7	42.4	32
QS2	Zn 4.5, Sb 2, Sn 1.	92.4 Ag, 4.4 Zn, 2.1 Sb, 1 Sn	890	do	9.98	37,000	77	10	42.4	40.5
QS3	Ni 3.5, Cu 2, Ta 1.5.	96.7 Ag, 2.2 Cu, 1 Ni, 0 Ta	------	do	10.42	34,500	48	7	38.1	53
98	Commercial tarnish-resisting silvers.	92.8 Ag, 3.4 Cd, 3.2 Sb	------	do	10.19	--------	------	-----	------	------
99		92.9 Ag, 0.4 Ni, 2.6 Cu, 3.9 Zn	------	do	10.25	--------	------	-----	------	------

(a) CHROMIUM ALLOYS

Attempts to dissolve in silver 2 per cent of chromium with 5 per cent of antimony, tin, zinc, or cadmium were made in alloys TS1 to TS4. The additions of metallic chromium were made to the molten binary silver alloy. Rather high temperatures, approximately 1,300° to 1,400° C., were required to secure any apparent solution of chromium in the silver-antimony or silver-tin melts while with silver-zinc and silver-cadmium rapid volatilization of zinc or cadmium occurred at these temperatures and little, if any, evidence of solution of chromium was noted. The analyses of the resulting ingots bore out these observations.

(b) NICKEL ALLOYS

Four attempts were made to dissolve nickel in silver with the aid of antimony, tin, zinc, or cadmium, alloys TS5 to TS8. Again rather high temperatures were required to obtain even a small proportion of nickel in the cast ingot. Alloy TS5 which showed the greatest proportion of nickel by analysis was not homogeneous, but showed numerous inclusions, probably of nickel. In preparing alloy TS19 a nickel-chromium alloy was added to molten silver, but with no evidence of solution of the nickel-chromium addition. The ingot was remelted with the addition of antimony, giving a final alloy containing 0.6 per cent of nickel, 0.1 per cent of chromium, and 1.6 per cent of antimony.

(c) MOLYBDENUM ALLOYS

Attempts to introduce molybdenum into silver were made in alloys TS9 to TS12 and TS14. Metallic molybdenum did not dissolve in a molter silver-antimony alloy heated to approximately 1,300° C. A 75 per cent aluminum, 25 per cent molybdenum alloy (prepared by melting in a graphite crucible at close to 2,000° C, and doubtless containing some carbon) appeared to dissolve in molten silver at a temperature probably above 1,500° C., but the resulting alloy was very hard and brittle (TS10). Alloys of manganese-molybdenum and nickel-molybdenum, each containing approximately 30 per cent of molybdenum, were made in zirconium oxide crucibles. Addition of these alloys to molten silver (alloys TS11 and TS12) resulted only in the solution of manganese or of nickel in the silver. The addition of zinc to the remelted ingot TS10 did result in a workable alloy (TS14) showing by analysis a molybdenum content of 0.3 per cent.

(d) TANTALUM ALLOYS

Alloys intended to contain tantalum were TS20, TS21, and QS3. Alloys of tantalum-antimony, tantalum-aluminum, and tantalum-nickel-copper were prepared by melting in zirconia crucibles and the resulting alloys added to molten silver. In all cases there was a considerable undissolved residue from the tantalum alloy addition and chemical analyses failed to detect tantalum in any of these three ingots.

(e) TERNARY AND QUATERNARY ALLOYS WITH A ZINC-SILVER BASE

The zinc-silver binary alloys were somewhat more easily prepared, of slightly better color, and slightly stronger than the corresponding cadmium-silver alloys. The zinc-silver alloy was, therefore, selected as the binary alloy base with which attempts should be made to improve mechanical properties by further alloying additions. It has already been shown that the tests of the binary alloys indicated the addition of antimony or of tin as suitable for increasing the strength of zinc-silver alloys. Alloy TS13 was accordingly made to contain 4.5 per cent of zinc and 2.5 per cent of antimony. It may be noted that this composition somewhat resembles that of the alloy "Silanca," previously mentioned, but that the proportions of zinc and antimony are reversed in TS13; that is, the base metal added primarily for increasing the tarnish resistance of silver, namely, zinc, is present in the greater proportion, while the antimony added primarily to increase strength is in the smaller amount. The majority of the available analyses of "Silanca" show the presence of greater amounts of antimony than of zinc or cadmium.

The addition to zinc-silver of tin as the hardening element was made in alloy TS16, of aluminum in TS15, and of magnesium in TS18. To satisfy a certain curiosity as to the effect of the presence of both a tarnish-inhibiting and a tarnish-promoting element in silver, TS17 was made to contain both zinc and tellurium.

Two quaternary alloys with the zinc-silver base were also made, QS1 to contain both antimony and aluminum as hardening additions, and QS2 to contain both antimony and tin.

(f) RECENTLY SUGGESTED TARNISH-RESISTANT SILVER COMPOSITIONS

After the completion of this investigation two silver alloy compositions were suggested as being tarnish resistant. The first was a silicon-cadmium-silver alloy [32] containing 4 per cent silicon and 3.5 per cent of cadmium, and the second was a sodium-zinc-silver alloy [33] containing 0.25 to 0.50 per cent of sodium and 6.5 per cent of zinc. Samples approximating these compositions were prepared for tarnish tests by the methods employed in this investigation.

The silicon-cadmium-silver alloy, TS22, was prepared by direct addition of the alloying metals to pure silver. The sodium-zinc-silver alloy, TS23, was made by adding to a molten zinc-silver alloy a previously prepared alloy of silver and sodium containing approximately 1 per cent of sodium. This sodium-silver alloy was made by adding gradually to molten silver the metallic sodium as small pellets wrapped in silver foil.

Corson has also reported [34] that an alloy of silver with about 15 per cent manganese and 5 per cent aluminum seems to be much less inclined to tarnish than pure silver or sterling silver. He does not give any further details.

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[32] M. G. Corson, Copper hardened by new method, Iron Age, **119**, pp. 421–424; 1927.

[33] Walter L. Mitchell, "Silver Alloy and Method of Making Same." United States Patent No. 1614752. Jan. 18, 1927.

[34] M. G. Corson, Manganese in nonferrous alloys. Mining and Metallurgy, Separate No. 1655–C–E, May; 1927.

(g) COMMERCIAL TARNISH-RESISTANT SILVERS

In Table 3, as alloys Nos. 98 and 99 are given the compositions of two specimens of foreign tarnish-resisting silver alloys, which are understood to have had some use in the silver trade.

2. MECHANICAL PROPERTIES

No detailed discussion is required of the mechanical properties of the ternary alloys intended to contain chromium, nickel, molybdenum, or tantalum. No alloying of the latter metal was obtained and only a slight alloying of molybdenum in one instance. It is probable also that a considerable proportion of the small amounts of chromium and nickel indicated by analyses of the ingots intended to contain these metals represented simply inclusions of a separate solid phase occasioned by the very rapid chilling of the small ingots as cast from extremely high temperatures.

The addition of antimony, tin, or aluminum, singly or in combination, to a zinc-silver alloy brought about increases in strength, which might be expected from the influence of the individual metals on the strength of silver. The greatest strengthening was obtained by the addition of aluminum, and next in order were antimony and tin. Antimony and tin together (2 per cent of antimony and 1 per cent of tin) in an alloy containing 4.5 per cent of zinc gave an alloy of as great strength as the zinc-silver alloy hardened with aluminum alone. These two alloys possessed the greatest strength of any of the workable silver alloys of approximately sterling fineness. All of the zinc-silver base alloys, with the exception of the alloy containing tellurium (TS17), were readily rolled cold to the regular 0.064-inch sheets.

The silicon-cadmium-silver alloy (TS22) was rolled hot (at approximately 700° C.) from the one-half-inch thick ingot to about one-eighth-inch thick plate when the alloy cracked along the edges and surface too much to continue rolling.

The sodium-zinc-silver alloy (TS23) showed many surface fissures after very little deformation in the cold rolls. However, tarnish test specimens were prepared from this alloy as thus slightly worked.

3. TARNISH RESISTANCE

The results of the tarnish tests of the ternary silver alloys are given in Table 4, and Figure 2 illustrates a set of tarnished test specimens. The gas-tarnish tests of these alloys were carried out in two groups shown separately as tests 6 and 7. The sodium polysulphide test was carried out on all alloys in a single test (No. 8) with the exception of the silicon-cadmium-silver and the sodium-zinc-silver alloys prepared subsequent to the testing of the other alloys and listed under tarnish test No. 11.

TABLE 4.—*Results of tarnish tests on ternary alloys of silver*

Tarnish test No.	Conditions of tarnish test	Predominant tarnish color of specimens after test [1]				
		Black	Purple	Brown	Yellow	Negligible
6	45 minutes; 2 per cent H_2S, 5 per cent SO_2, moist air.	7.5 Cu [2] (0 Al, 0 Mo) [3]	4 Mn, (0 Mo) [3] 2; 4 Mn [2] 1.3 Ni (0 Mo) [3] 2 Ni [2] Pure silver.	4.5 Cd, 0.5 Ni 4.7 Zn, 0.6 Ni	5 Zn [2] 4.7 Zn, 0.2 Cr 5.6 Sn, 0.8 Ni 4.7 Cd, 0.06 Cr 5.2 Sn, 1 Cr 5.3 Zn (2.1 Al, 0.3 Mo) [3] 3.5 Sb, 1 Ni 5.3 Sb, 1.2 Cr 4.6 Zn, 2.7 Sb	
7	Same as previous test.	7.5 Cu [2]	2.2 Cu, 1 Ni (0 Ta) [3]	(0 Al, 0 Ta) [3]	1.6 Sb, 0.6 Ni, 0.1 Cr 3.5; 5; 7.5 Zn [2] 5.2 Zn, 1.9 Mg 3.1 Sb (0 Ta) [3] 5.2 Zn, 2 Sn	4.4 Zn, 2.1 Sb, 1 Sn 4.5 Zn, 2.1 Sb, 0.7 Al 4.6 Zn, 2.7 Sb 4.5 Zn, 2.3 Al
8	8 minutes; sodium polysulphide.	2.2 Cu, 1 Ni (0 Ta) [3] 0.6 Ni, 1.6 Sb, 0.1 Cr (0 Al, 0 Ta) [3] 1.3 Ni (0 Mo) [3] Al, Mo [4]	------------	4.5 Cd, 0.5 Ni 3.5 Sb, 1 Ni 4 Mn, (0 Mo) [3] 3.1 Sb (0 Ta) [3] 3.4 Cd, 3.2 Sb 2.6 Cu, 3.9 Zn, 0.4 Ni 4.5 Zn, 2.3 Al	4.7 Zn, 0.6 Ni 4.7 Cd, 0.06 Cr 5.6 Sn, 0.8 Ni 5.3 Sb, 1.2 Cr 4.5 Zn, 2.1 Sb, 0.7 Al	5.3 Zn (2.1 Al, 0.3 Mo) [3] 5.2 Sn, 1 Cr 4.6 Zn, 2.7 Sb 4.7 Zn, 0.2 Cr 4.4 Zn, 2.1 Sb, 1 Sn 5.2 Zn, 1.9 Mg 5.2 Zn, 2 Sn
11	8 minutes; sodium polysulphide.	------------	Pure silver.	3.2 Si, 4.1 Cd 10 Cd [2] Na, 7 Zn <0.1	7.5 Zn [2]	4.6 Zn, 2.7 Sb 20 Cd [2] 20 Zn [2]

[1] Within each block of the table the alloys are arranged in the approximate order of decreasing tarnish.

[2] Binary alloys.

[3] Parentheses indicate that the alloy intended to contain the metals indicated either failed to show their presence by analysis or, if shown, they were present probably as inclusions.

[4] No analysis.

In these tests again, as in the tarnish tests of binary alloys, the presence of copper, nickel, or manganese promotes the tarnishing of the alloy except in those alloys in which the effect of the tarnish-promoting element is outweighed by larger proportions of antimony, tin, cadmium, or zinc. The alloys containing approximately 5 per cent of zinc with 2 or 3 per cent of antimony or tin, or of antimony and tin combined were the most consistently tarnish-resistant alloys as judged on the basis of both types of tarnish tests. The silver-zinc alloys containing either aluminum or magnesium as the hardening element are indicated as somewhat more susceptible to tarnishing than similar alloys hardened with antimony or tin, as in the sodium polysulphide test the silver-zinc and silver-zinc-antimony alloys containing aluminum were rather heavily tarnished although they had been rather resistant in the gas-tarnish test. In somewhat the same way silver-zinc hardened with magnesium was appreciably tarnished in the gas test, although it was one of the best alloys in resistance to tarnish in the polysulphide solution. The presence of small amounts of chromium in silver-antimony, silver-tin, and silver-zinc had no apparent influence on the degree of tarnish. These specimens tarnished to about the same extent and relative degree as the corresponding binary alloys without chromium.

The silicon-cadmium-silver alloy tarnished in comparison with several control specimens in test No. 11, darkened somewhat less than pure silver, but appreciably more than the 20 per cent cadmium or zinc binary alloys and the " reversed silanca " composition containing 4.6 per cent zinc and 2.7 per cent antimony. The position of the silicon-cadmium-silver alloy would then appear to be that to be expected from its cadmium content and to be little, if any, changed by the presence of silicon.

The position of the sodium-zinc-silver alloy in this same tarnish series was nearly the same as that of the silicon-cadmium-silver alloy. Its position, too, is that to be expected from its zinc content alone. However, this alloy was peculiar in that its tarnish film was quite readily removed with a moist cloth or the moistened finger tip. The tarnish film upon the zinc-silver alloy containing no sodium could not be thus removed.

4. SUMMARY OF PROPERTIES OF TERNARY ALLOYS

The outstanding tarnish-resistant compositions of the ternary alloys prepared were the zinc-silver base alloys hardened with antimony (TS13), with tin (TS16), or with both antimony and tin (QS2). The tensile strength of the silver-zinc-antimony-tin alloy is the highest of these three compositions, namely, 37,000 lbs./in.^{2} This value is to be compared with 44,000 lbs./in.^{2} tensile strength for copper-silver of sterling fineness. The silver-zinc-antimony alloy had a strength of 35,000 lbs./in.^{2} and the corresponding silver-zinc-tin alloy, 32,000 lbs./in.^{2} All three of these alloys were quite easily rolled cold to sheets. The silver-zinc-antimony alloy, however, appeared to be somewhat more liable to develop imperfections in the sheets than the other two alloys. In other cases, also, alloys containing antimony exhibited this same tendency to roll a little less readily than the corresponding alloys containing tin.

VIII. ALLOYS CONTAINING GOLD

1. PREPARATION AND PHYSICAL PROPERTIES

The final series of alloys prepared in this investigation was of several compositions containing gold. These alloys were prepared in smaller lots (about 100 g each) and were cast in ingots approximately 3 inches long, by 13/16 inch wide, by 3/16 inch thick.

The chief points of interest in the preparation of silver alloys containing gold were first to determine if gold exhibited any tendency to retard the tarnish of silver; second, to add gold to certain of the very tarnish-resistant binary alloys, that is, those containing 20 to 25 per cent cadmium or zinc, in order to offset the possible objection to such alloys on the basis of their lower intrinsic value as compared with alloys of sterling fineness; and finally to make a still further attempt to alloy chromium and nickel with silver with the assistance of considerable proportions of gold.

The compositions and physical properties of silver alloys containing gold are given in Table 5. No particular comments need be made in regard to the preparation of these alloys except in the case of the silver-gold-chromium alloys. A gold-chromium alloy was prepared by mixing fine filings of gold and chromium, compressing the filings to briquets, annealing the briquets in hydrogen at 1,000° C. for four hours, and finally raising the temperature to a little over 1,200° C. The alloy thus obtained was remelted in a zirconia crucible under hydrogen and then added in the desired amounts to molten silver.

TABLE 5.—*Composition and physical properties of silver alloys containing gold*

Alloy No.	Composition		Freezing point	Color of alloy (polished surface)	Density at 25° C.	Tensile strength of annealed sheets	Elongation in 1.0 inch	Hardness			
	Intended alloying metal, per cent	Found by analysis, per cent						Ingot as cast: Scleroscope	Ingot as cast: Brinell	Annealed sheet: "Baby Brinell"	Rolled sheet: Baby "Brinell"
			° C.		*g/cm³*	*Lbs./in.²*	*Per cent*				
G1	75 Au	------	1,030	Yellow	16.05	27,500	45	2	28.4	40	96
G2	50 Au	------	1,010	Water green.	13.62	26,000	50	10	------	44	117
G3	20 Au	------	980	White	11.63	23,500	66	3	32.8	34	93.5
G4	7.5 Au	------	------	do	10.87	21,500	36	1.5	24.8	29	74.4
G5	5 Au, 2 Al	92.8 Ag, 5.1 Au, 1.9 Al	------	do	10.19	38,000	64	8	36.2	48	105
G6	5 Au, 2 Cd	92.7 Ag, 5.1 Au, 2.2 Cd	950	do	10.72	24,000	50	2.5	24.8	40	81
G7	5 Au, 2 Sb	92.8 Ag, 5.2 Au, 2 Sb	950	do	10.68	26,500	67	5.5	29.8	44	111
G8	20 Au, 25 Cd	59.1 Ag, 21.5 Au, 19.4 Cd	860	Slight yellow.	11.36	40,000	66	36.5	34.4	59	130
G9	20 Au, 15 Zn	65.8 Ag, 20.2 Au, 14 Zn	770	do	10.80	48,000	67	11.5	47.5	72	155
G10	7 Au, 0.5 Cr	92.5 Ag, 7.2 Au, 0.3 Cr	------	White	10.83	27,500	44	2	25.8	55	69
G11	12 Au, 0.9 Cr	84.2 Ag, 15.4 Au, 0.4 Cr	------	do	11.21	------	------	3	29.8	45	96
G12	23 Au, 1.6 Cr	66.6 Ag, 32.8 Au, 0.6 Cr	------	do	12.18	------	------	------	------	77.8	103
G13	8 Au, <2 Ni	90.7 Ag, 8.5 Au, 0.7 Ni	------	do	10.87	------	------	6	33.6	------	103
G14	8 Au, 2 Ni	89.7 Ag, 8.4 Au, 1.8 Ni	------	do	10.85	------	------	4	32.8	50	105
G15	0.6 Au, 20 Zn	79.4 Ag, 0.6 Au, 20 Zn	------	Slight yellow.	9.69	------	------	7.5	38.1	36	122
G16	4 Au, 36 Zn	------	------	Steel gray [1]	------	------	------	17	69.1	------	------
B2	5 Au, 2.5 Be	92.4 Ag, 6 Au, 1.6 Be	------	Gray	9.91	------	------	14	73.8	------	103
S2	Pure Ag	------	960	White	10.49	[2] 21,500	53	1	22.8	29	70.5

[1] Changed to pink on standing.

[2] Lower value than obtained from 300 g ingot probably due to less rolling of 100 g ingot.

Gold had little tendency to strengthen silver either in the binary silver-gold alloys (G1 to G4) or in the ternary alloys containing 5 per cent of gold with 2 per cent of cadmium or antimony. Alloys G8 and G9 were made up without regard to the maintenance of sterling fineness. They contained, respectively, 20 per cent of cadmium and 15 per cent of zinc each with 20 per cent of gold. In these specimens the gold had a very noticeable influence on the mechanical properties of the alloys, increasing the strength and hardness with but little lowering of the elongation as compared with the values for the binary alloys of corresponding cadmium and zinc contents. These two alloys more nearly corresponded to sterling silver in tensile strength, elongation, and hardness than any of the more tarnish-resisting alloys previously prepared in this investigation.

The intrinsic value of alloys G8 or G9 was, of course, much greater than sterling silver. In alloy G15 just sufficient gold was added to a silver-zinc containing 20 per cent of zinc to give an alloy of intrinsic value equivalent to sterling silver.

Alloy B2, in which gold was added to silver-beryllium in the attempts to secure a workable alloy, could be deformed slightly in the rolls without breaking the small ingot, but could not be rolled to a sheet.

2. TARNISH RESISTANCE

The tarnish-test results on the silver alloys containing gold are given in Table 6 and the tarnished specimens illustrated in Figure 2. These results indicate that gold has about the same effect as an equal weight per cent of zinc in reducing the tarnish of silver in that a 7.5 per cent gold-silver alloy in both tarnish tests 9 and 10 was slightly less tarnishing than the 5 per cent silver-zinc alloy.

TABLE 6.—*Results of tarnish tests on silver alloys containing gold*

Tarnish-test No.	Conditions of tarnish test	Predominant tarnish color of specimens after test [1]				
		Black	Purple	Brown	Yellow	Negligible
9	45 minutes; 2 per cent H_2S, 5 per cent SO_2, moist air.	2.5 Be	7.5 Cu	1.6 Be, 6 Au	Pure silver 5 Zn 5 Au, 2 Cd 7 Au, 0.3 Cr 4.5 Zn, 2.5 Sb 5 Au, 2 Al 7.5 Au 8 Au, 2 Ni 8 Au, 0.7 Ni 0.6 Au, 20 Zn 15 Au, 0.4 Cr 33 Au, 0.6 Cr 5 Au, 2 Sb	20 Au 20 Au, 20 Cd 20 Au, 15 Zn 50 Au 75 Au
10	8 minutes; sodium polysulphide.	1.6 Be, 6 Au	2.5 Be 7.5 Cu Pure silver 8 Au, 2 Ni	8 Au, 0.7 Ni 5 Au, 2 Al 33 Au, 0.6 Cr 5 Au, 2 Sb	5 Zn 4.5 Zn, 2.5 Sb 7 Au, 0.3 Cr 5 Au, 2 Cd 7.5 Au 15 Au, 0.4 Cr 20 Au	0.6 Au, 20 Zn 20 Au, 20 Cd 20 Au, 15 Zn 50 Au 75 Au

[1] Within each block of the table the alloys are arranged in the approximate order of decreasing tarnish.

The silver-gold alloys containing nickel were not appreciably more resistant to tarnish than a corresponding silver-gold binary alloy containing no nickel. Likewise, the alloys containing small amounts of chromium were no more tarnish resistant than the similar alloys without chromium.

The alloys high in both gold and cadmium or zinc, and the gold-zinc alloy made to have the intrinsic value of sterling silver, were very resistant to tarnish, although not noticeably more resistant than alloys of similar base-metal content containing no gold. The alloys high in gold, however, did appear to roll to sheet more readily and to give sheets having better surfaces. It must be recalled, however, that only a very limited trial of the working qualities of these alloys was made in the present investigation.

IX. ELECTROPLATED SILVER ALLOYS

A number of references in the literature to the electrodeposition of silver alloys, particularly silver-cadmium alloys[35] suggested attempts to electroplate some of the more tarnish-resisting of the binary alloys tested in this investigation, namely, the zinc-silver or cadmium-silver alloys.

A few preliminary trials were made to electroplate zinc-silver and cadmium-silver alloys.[36] Alloys of cadmium-silver containing approximately 5 and 8 per cent cadmium were secured. The deposition of such alloys, however, requires extremely careful control of plating conditions in order to give an alloy of predetermined composition. Very slight changes in current density caused large changes in the composition of the deposited alloy. It would thus be very difficult to plate an irregular object with an alloy of uniform composition.

The preliminary attempts to electroplate an alloy of zinc and silver were unsuccessful. As far as is evident from present available data there is not much promise of being able to electroplate zinc-silver alloys.

X. MISCELLANEOUS TARNISH TESTS

A few trials were made of some suggested methods of tarnishing silver specimens other than the gas test and sodium sulphide test regularly used.

One of these additional tests was to stick the ends of tarnish specimens in the crushed yolks of eggs boiled for 30 minutes. Another test consisted of wrapping rubber bands around polished tarnish specimens. Still a third suggested test was to allow the specimens to remain in contact with free sulphur. All of these tests appeared to be quite severe and provided but little differences in color of the tarnish film. All specimens in the free sulphur tarnish tests, for example, had gray and black tarnish films which had to be judged on the basis of the depth of a single color only and were not as readily arranged in order of degree of tarnish as were the same specimens in the gas or the sodium sulphide test. These miscellaneous tests confirmed the choice of the two tarnishing methods used throughout the work as the more convenient of the usual methods of tarnishing.

Care must be taken in all tarnish tests of silver alloys not to use a given specimen of an alloy for a second tarnish test if the original

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[35] W. R. Ingalls, Metallurgy of Zinc and Cadmium, 1906, p. 593. N. F. Budgen, Cadmium, Its Metallurgy, Properties, and Uses, 1924, pp. 200–219. A. H. W. Aten and M. F. Van Putten, Electrodeposition of silver-cadmium alloys, Rec. Trav. Chim., **44**, p. 861; 1925.

[36] We are indebted to W. Blum, of the division of chemistry, for all electroplating tests.

tarnish film has been removed simply by a light polishing or buffing. In some alloy compositions it is very noticeable that a polished surface once tarnished and then cleaned by light buffing is thereby very much changed in the ease with which it tarnishes a second time. If it is desirable to use a given series of tarnished specimens for a second test the polished test surfaces should be ground down rather deeply and then repolished to avoid this difficulty.

A copper-silver alloy after an initial tarnish followed by a light buffing tarnishes less heavily than in its original condition, while a zinc-silver alloy tarnishes more heavily after a similar treatment. Both of these alloys thus approach pure silver in their resistance to tarnish after successive exposures. Such behavior indicates a removal of the base metal from the surface of the silver alloy by successive tarnishing and cleaning and results in silver-enriched surfaces. It is therefore to be expected that at least some of the silver alloys, which on initial tarnishing tests are very noticably more or less tarnished than pure silver, may after continued use and cleaning be less widely separated and more closely approach pure silver in their tarnish-resistant qualities.

XI. SUMMARY AND CONCLUSIONS

As one phase of the technical research undertaken at the direction of the United States Commission on Gold and Silver Inquiry, with a view to increasing the uses of silver, a wide variety of silver alloys were made, certain of their physical and mechanical properties were determined, and polished specimens were subjected to accelerated sulphur-tarnishing tests.

Alloys of silver with cadmium or zinc were the most tarnish resistant of the binary alloys. These alloys were readily rolled to sheets, but were of the lowest tensile strength of all the workable binary alloys.

Antimony and tin were rather effective in strengthening silver in binary combinations and at the same time showed some tendency to increase the tarnish resistance of silver, although not to so great a degree as cadmium or zinc. The addition of either antimony or tin, or of both antimony and tin to a silver-zinc alloy, the sum of all alloying metals not exceeding 7.5 per cent in order to give alloys of sterling fineness, produced workable alloys of marked tarnish resistance and of greater strength than any of the tarnish-resistant binary alloys.

Alloys of silver with 15 or 20 per cent of zinc or cadmium and 20 per cent of gold were very easily worked, possessed strength and hardness values more nearly comparable to copper-silver of sterling fineness than any of the other alloys prepared, and at the same time were very tarnish resistant. The debasement of silver by the addition of 15 to 20 per cent of base metal was more than offset in these alloys by the high gold content.

None of the alloys made and tested in the investigation can be described as "nontarnishing." All could be tarnished under sufficiently severe conditions. Many of them, however, were distinctly more resistant to laboratory sulphur-tarnish tests than ordinary sterling silver.

While the relative tarnish resistance of silver alloys under the conditions of household use may not exactly parallel the results of laboratory tests it is a reasonable presumption that the labor required to keep in presentable condition ware made from the more tarnish-resistant silver alloys named above would be less than that required for ware made of the ordinary copper-silver alloy of sterling fineness.

Many of the tarnish-resistant alloys are of such properties as probably to be workable into most of the articles now made of sterling silver and to have satisfactory strength and resistance to scratching. Somewhat greater care would be required in some cases in manufacturing articles requiring soldering since certain of the tarnish-resistant alloys, particularly those high in zinc or cadmium, have lower melting points than ordinary sterling silver.

Tarnish-resistant silver alloys high in cadmium or zinc and of acceptable appearance could be produced at a lower cost for the constituent metals than is the case for sterling silver. The lower cost of the constituent metals, however, is only a part of the total cost of the manufactured silver articles and it is questionable whether any wider use of silverware and increased consumption of silver would result from the introduction of such alloys of intrinsic value lower than sterling silver. In a plant producing both sterling silver and a tarnish-resisting silver the difficulties involved in handling two alloys of similar appearance, but of different compositions, might become rather serious and add appreciably to the cost of production.

There has been built up in the public mind a strong sentiment in favor of the sterling standard as a safeguard of the intrinsic worth of silverware, a fact which must be kept in mind in a consideration of the commercial possibilities of new silver alloys for most purposes. There are, however, minor uses for silver alloys where the maintenance of sterling fineness is of no consequence and the increased resistance to tarnish of alloys of lower fineness would be a very appreciable advantage. Such would be the case, for example, in the use of silver for the graduated scales of scientific instruments and metallic wires and ribbons for the insignia and decorations of military and fraternal uniforms. Tarnish-resistant alloys at present under test in a commercial laboratory for use in certain types of electrical contacts have given promise of better service than the pure silver contacts previously used.

An absolutely nontarnishing silver alloy, of suitable properties in other respects, would quite certainly have commercial possibilities. Since, however, an extensive survey of silver alloys has revealed no such nontarnishing composition and has indicated that the development of such an alloy is rather unlikely, there seems to be little opportunity for an immediate revolution in the silver industry by means of the introduction of a nontarnishing alloy. Whether the improvement in tarnish-resistant properties such as can be obtained by some of the alloys described herein would be of sufficient value to the user to justify their manufacture and introduction to the trade in the face of the present demand for sterling and of the uncertainty as to the difficulties in the manufacture of new alloy compositions can only be determined by actual trial. But if any such commercial development is undertaken it should be made unmistakably clear to the consumer that the alloys are only tarnish resistant and not completely nontarnishing.

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