

The Quantitative Determination of the Degree of Tarnishing of a Metallic Surface by its Reflective Power.

By

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The polished surface of ordinary metals and alloys get tarnished if they are left open to the air, but for the degree of tarnishing there has been known no adequate method of measurement. Applying the principle of measuring the reflective power as described in my former paper,¹ I have devised a new method, which runs as follows:—

The samples, which have been measured for their reflective powers directly after polishing, are allowed to stand 24 hours in a special room containing specified quantities of moisture and carbon dioxide, and then again measured for their reflective powers now diminished. The ratio between both determinations gives the degree of tarnishing.

This method has been applied to the alloys of the systems, copper and silver, copper and cadmium, tin and cadmium, bismuth and cadmium, and bismuth and tin. The numerical data together with the graphs are given in the following pages:—

¹ These memoirs, A, **11**, 43 (1928).

A. System of Copper and Silver

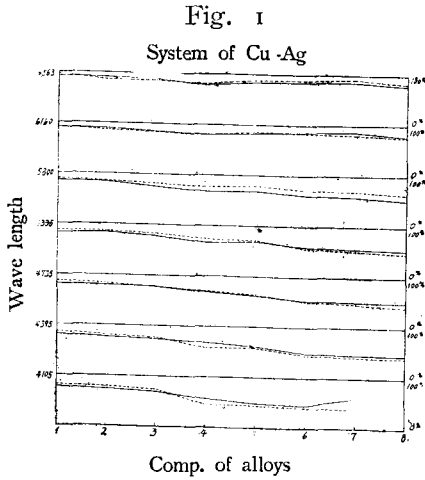
Table I
 Reflective Power of the Alloys of Copper and Silver
 a. Immediately after Polishing

| No. | Sample | | Reflective power in % for wave length | | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | 4105 |
| | Cu in % | Ag in % | | | | | | | |
| 1 | 100 | 0 | 95.71 | 91.30 | 89.28 | 87.70 | 87.36 | 85.88 | 82.02 |
| 2 | 98 | 2 | 90.75 | 86.70 | 85.88 | 85.50 | 83.88 | 81.61 | 78.26 |
| 3 | 85 | 15 | 90.12 | 83.08 | 82.81 | 82.42 | 78.67 | 77.50 | 73.96 |
| 4 | 72 | 28 | 81.80 | 79.66 | 77.86 | 73.21 | 70.05 | 59.97 | 46.60 |
| 5 | 50 | 50 | 88.61 | 86.43 | 78.90 | 72.09 | 64.30 | 58.73 | 44.65 |
| 6 | 20 | 80 | 89.75 | 84.49 | 71.48 | 56.71 | 50.32 | 45.01 | 40.81 |
| 7 | 10 | 90 | 92.61 | 81.80 | 69.41 | 51.80 | 47.33 | 42.65 | 38.35 |
| 8 | 0 | 100 | 82.79 | 75.65 | 63.20 | 47.30 | 42.76 | 40.31 | |

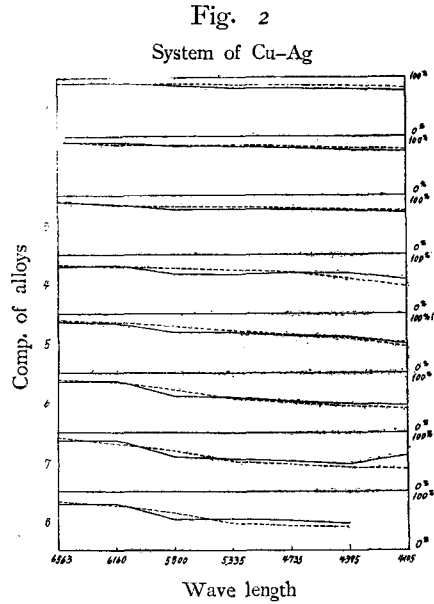
b. After standing in a room at 14° C. with 4.8 % CO₂¹ by volume and 13.66 moisture² in terms of relative humidity

| No. | Sample | | Reflective power in % for wave length | | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | 4105 |
| | Cu in % | Ag in % | | | | | | | |
| 1 | 100 | 0 | 91.03 | 91.57 | 85.81 | 82.42 | 81.09 | 81.24 | 77.38 |
| 2 | 98 | 2 | 90.13 | 90.01 | 84.31 | 84.32 | 80.00 | 77.70 | 74.17 |
| 3 | 85 | 15 | 89.08 | 85.60 | 75.10 | 77.52 | 76.06 | 74.81 | 70.53 |
| 4 | 72 | 28 | 79.80 | 81.35 | 67.60 | 66.17 | 68.28 | 68.86 | 57.90 |
| 5 | 50 | 50 | 85.60 | 83.83 | 68.57 | 68.10 | 63.32 | 60.48 | 48.44 |
| 6 | 20 | 80 | 85.00 | 87.73 | 60.95 | 58.47 | 52.61 | 17.44 | 45.84 |
| 7 | 10 | 90 | 86.06 | 87.07 | 58.70 | 55.78 | 52.02 | 46.89 | 42.78 |
| 8 | 0 | 100 | 73.36 | 79.05 | 52.30 | 53.12 | 50.10 | 45.24 | |

- 1 The determination of carbon dioxide was made from the decrease of the volume of the air after absorbing carbon dioxide in a caustic soda solution: *vide* Scott's "Method of Air Analysis", 1912, p. 62.
- 2 The determination of moisture was made from the increase of the weight of a dry pumice-stone after passing a definite volume of air: Scott's "Method of Air Analysis", p. 95.



Comp. of alloys
Reflective power after standing in full line.
Reflective power before standing in dotted line.



Wave length
Reflective power after standing in full line.
Reflective power before standing in dotted line.

B. System of Copper and Cadmium

Table III

Reflective Power of the Alloys of Copper and Cadmium.
a. Immediately after Polishing

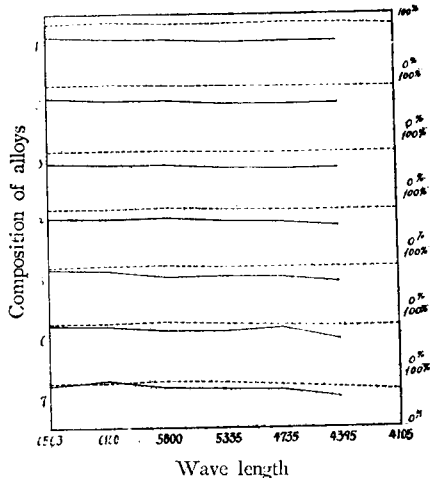
| No. | Sample | | Reflective power in % for wave length | | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | 4105 |
| | Cu in % | Cd in % | | | | | | | |
| 1 | 0 | 100 | 83.95 | 85.92 | 84.15 | 84.75 | 86.18 | 85.34 | 82.18 |
| 2 | 0.5 | 99.5 | 80.04 | 81.60 | 80.24 | 79.44 | 78.40 | 78.05 | 77.41 |
| 3 | 1.1 | 98.9 | 68.73 | 69.56 | 69.49 | 67.05 | 66.82 | 66.69 | 66.37 |
| 4 | 5.0 | 95.0 | 71.84 | 71.99 | 73.37 | 70.50 | 69.39 | 69.11 | 68.54 |
| 5 | 10.0 | 90.0 | 72.92 | 73.26 | 74.21 | 72.78 | 72.45 | 72.18 | 71.83 |
| 6 | 20.0 | 80.0 | 76.25 | 77.46 | 79.04 | 76.19 | 73.66 | 72.72 | 72.11 |
| 7 | 27.7 | 72.3 | 75.18 | 76.27 | 78.67 | 75.95 | 71.88 | 67.76 | 61.69 |

b. After standing in a room at 14° C. with 4.8 %
CO₂ by volume and 13.66 moisture
in terms of relative humidity

| No. | Sample | | Reflective power in % for wave length | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 |
| | Cu in % | Cd in % | | | | | | |
| 1 | 0 | 100 | 60.17 | 58.76 | 57.02 | 53.28 | 54.29 | 54.69 |
| 2 | 0.5 | 99.5 | 59.00 | 54.69 | 54.92 | 49.92 | 48.18 | 48.28 |
| 3 | 1.1 | 98.9 | 48.32 | 45.93 | 46.97 | 40.69 | 37.36 | 38.59 |
| 4 | 5.0 | 95.0 | 55.30 | 54.69 | 56.70 | 50.29 | 48.17 | 42.34 |
| 5 | 10.0 | 60.0 | 69.95 | 66.41 | 55.43 | 67.41 | 55.84 | 46.94 |
| 6 | 20.0 | 80.0 | 74.04 | 72.37 | 65.42 | 64.40 | 68.17 | 48.55 |
| 7 | 27.4 | 72.3 | 72.96 | 79.29 | 68.60 | 66.79 | 64.06 | 50.82 |

Fig. 4

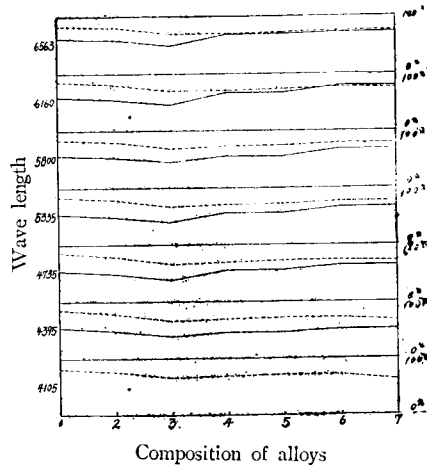
System of Cu-Cd



Reflective power after standing
in full line.
Reflective power before stand-
ing in dotted line.

Fig. 3

System of Cu-Cd



Reflective power after standing
in full line.
Reflective power before stand-
ing in dotted line.

C. System of Tin and Cadmium

Table V

Reflective Power of the Alloys of Tin and Cadmium

a. Immediately after Polishing

| Sample | | Reflective power in % for wave length | | | | | | | |
|--------|-------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| No. | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | 4105 |
| | Sn in % | Cd in % | | | | | | | |
| 1 | 0 | 100 | 83.95 | 85.92 | 84.15 | 84.75 | 86.18 | 85.34 | 82.18 |
| 2 | 15 | 85 | 77.45 | 66.89 | 65.86 | 63.21 | 57.00 | 61.83 | 57.96 |
| 3 | 35 | 65 | 42.00 | 40.87 | 35.16 | 37.97 | 31.74 | 34.28 | 32.16 |
| 4 | 68.7 | 31.3 | 23.87 | 35.86 | 27.52 | 24.98 | 21.04 | 25.62 | 22.97 |
| 5 | 85 | 15 | 41.52 | 49.07 | 37.77 | 34.18 | 31.87 | 33.26 | 31.03 |
| 6 | 93 | 7 | 56.57 | 62.69 | 51.19 | 35.26 | 33.63 | 36.97 | 34.35 |
| 7 | 100 | 0 | 73.14 | 78.10 | 70.91 | 67.52 | 57.10 | 61.81 | 59.34 |

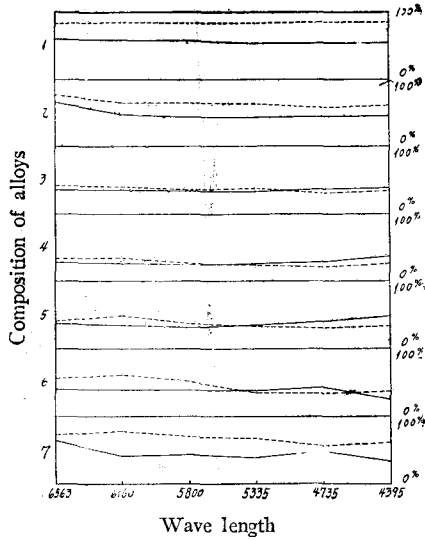
b. After standing in a room at 26° C. with 3.4 %

CO₂ and 76.19 moisture in terms of

relative humidity

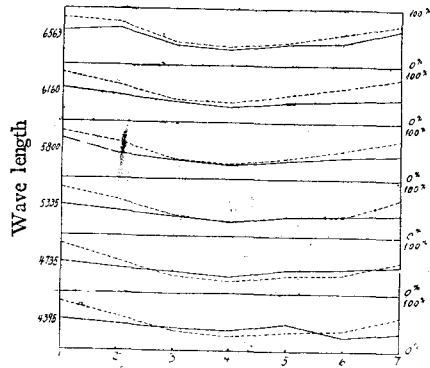
| Sample | | Reflective power in % for wave length | | | | | | | |
|--------|-------------|---------------------------------------|-------|-------|-------|-------|-------|-------|--|
| No. | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | |
| | Sn in % | Cd in % | | | | | | | |
| 1 | 0 | 100 | 60.17 | 58.76 | 57.02 | 53.28 | 54.59 | 54.69 | |
| 2 | 15 | 85 | 66.96 | 48.46 | 44.63 | 44.12 | 44.61 | 46.05 | |
| 3 | 35 | 65 | 36.98 | 36.25 | 33.91 | 34.71 | 37.61 | 38.98 | |
| 4 | 68.7 | 31.3 | 28.90 | 27.62 | 24.56 | 25.71 | 29.34 | 36.79 | |
| 5 | 85 | 15 | 37.78 | 35.36 | 32.67 | 35.13 | 41.50 | 47.35 | |
| 6 | 93 | 7 | 40.05 | 39.44 | 39.46 | 37.86 | 43.98 | 25.63 | |
| 7 | 100 | 0 | 64.78 | 42.10 | 43.34 | 39.69 | 49.91 | 33.52 | |

Fig. 6
System of Cd-Sn



Reflective power after standing
in *full* line.
Reflective power before stand-
ing in *dotted* line.

Fig. 5
System of Cd-Sn



Composition of alloys
Reflective power after standing
in *full* line.
Reflective power before stand-
ing in *dotted* line.

D. System of Bismuth and Cadmium.

Table VII

Reflective Power of the Alloys of Bismuth and Cadmium
a. Immediately after Polishing

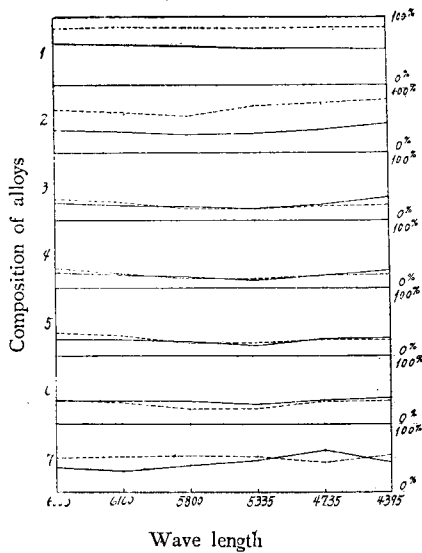
| No. | Sample | | Reflective power in % for wave length | | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4738 | 4395 | 4105 |
| | Cd in % | Bi in % | | | | | | | |
| 1 | 100 | 0 | 83.95 | 85.92 | 84.15 | 84.75 | 86.18 | 85.34 | 82.18 |
| 2 | 81 | 19 | 64.79 | 60.03 | 54.33 | 69.43 | 74.39 | 79.95 | 76.65 |
| 3 | 62 | 38 | 31.50 | 27.22 | 17.37 | 17.96 | 21.55 | 23.07 | 20.19 |
| 4 | 40 | 60 | 29.11 | 21.96 | 13.79 | 13.86 | 18.19 | 21.40 | 17.63 |
| 5 | 26 | 74 | 34.27 | 30.55 | 19.78 | 19.78 | 24.21 | 24.69 | 21.32 |
| 6 | 13 | 87 | 35.00 | 31.26 | 22.07 | 22.80 | 33.73 | 34.86 | 30.27 |
| 7 | 0 | 100 | 60.75 | 52.31 | 53.48 | 51.25 | 44.68 | 55.91 | 54.72 |

b. After standing in a room at 26° C. with 3.4 % CO₂ and 76.19 moisture in terms of relative humidity

| No. | Sample | | Reflective power in % for wave length | | | | | |
|-----|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|
| | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 |
| | Cd in % | Bi in % | | | | | | |
| 1 | 100 | 0 | 60.17 | 58.76 | 57.02 | 53.28 | 54.59 | 54.69 |
| 2 | 81 | 19 | 33.23 | 31.85 | 27.91 | 28.23 | 34.98 | 43.31 |
| 3 | 62 | 38 | 25.91 | 22.46 | 20.57 | 17.85 | 23.67 | 35.16 |
| 4 | 40 | 60 | 22.81 | 18.75 | 16.88 | 11.80 | 18.87 | 26.29 |
| 5 | 26 | 74 | 24.00 | 23.15 | 21.22 | 15.29 | 25.30 | 27.96 |
| 6 | 13 | 87 | 34.74 | 33.72 | 33.12 | 29.66 | 35.61 | 38.06 |
| 7 | 0 | 100 | 36.03 | 30.56 | 40.25 | 46.74 | 62.51 | 43.72 |

Fig. 8

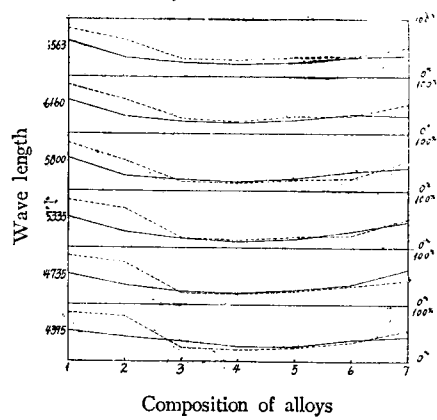
System of Bi-Cd



Reflective power after standing in full line.
 Reflective power before standing in dotted line.

Fig. 7

System of Bi-Cd



Composition of alloys
 Reflective power after standing in full line.
 Reflective power before standing in dotted line.

E. System of Bismuth and Tin.

Table IX

Relative Power in the Alloys of Bismuth and Tin

a. Immediately after Polishing

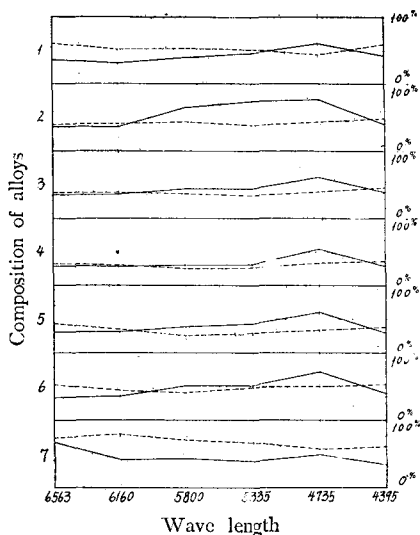
| Sample | | | Reflective power in % for wave length | | | | | | |
|--------|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| No. | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | 4105 |
| | Sn in % | Bi in % | | | | | | | |
| 1 | 0 | 100 | 60.75 | 52.31 | 53.48 | 51.25 | 44.68 | 59.91 | 54.72 |
| 2 | 13 | 87 | 39.35 | 41.60 | 44.16 | 38.64 | 43.63 | 49.02 | 44.79 |
| 3 | 27 | 73 | 38.77 | 38.46 | 37.53 | 34.18 | 40.89 | 46.78 | 42.32 |
| 4 | 42 | 58 | 32.09 | 31.27 | 25.30 | 27.24 | 33.18 | 37.21 | 31.68 |
| 5 | 62 | 38 | 43.27 | 35.07 | 26.88 | 29.00 | 34.70 | 38.67 | 32.96 |
| 6 | 81 | 19 | 52.92 | 44.79 | 41.32 | 48.32 | 50.67 | 58.30 | 54.27 |
| 7 | 100 | 0 | 73.14 | 78.10 | 70.91 | 67.52 | 57.10 | 61.81 | 59.34 |

b. After standing in a room at 26° C. with 3.4 %
CO₂ and 76.19 moisture in terms of
relative humidity

| Sample | | | Reflective power in % for wave length | | | | | | |
|--------|-------------|---------|---------------------------------------|-------|-------|-------|-------|-------|--|
| No. | Composition | | 6563 | 6160 | 5800 | 5335 | 4735 | 4395 | |
| | Sn in % | Bi in % | | | | | | | |
| 1 | 0 | 100 | 36.03 | 30.56 | 40.25 | 46.74 | 62.51 | 43.72 | |
| 2 | 13 | 87 | 36.73 | 36.79 | 65.11 | 74.35 | 77.36 | 40.24 | |
| 3 | 27 | 73 | 35.84 | 36.48 | 43.05 | 44.64 | 62.35 | 38.96 | |
| 4 | 42 | 58 | 28.47 | 28.72 | 30.80 | 32.30 | 54.83 | 29.66 | |
| 5 | 62 | 38 | 30.27 | 32.91 | 39.36 | 43.57 | 50.29 | 30.66 | |
| 6 | 81 | 19 | 33.57 | 36.36 | 51.10 | 52.63 | 72.39 | 40.18 | |
| 7 | 100 | 0 | 64.78 | 42.10 | 43.34 | 39.69 | 49.91 | 33.52 | |

Fig. 10

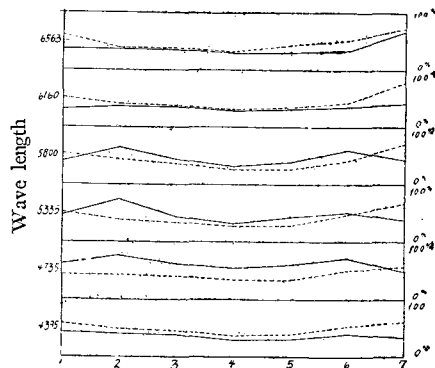
System of Bi-Sn



Reflective power after standing in *full* line.
 Reflective power before standing in *dotted* line.

Fig. 9

System of Bi-Sn



Composition of alloys
 Reflective power after standing in *full* line.
 Reflective power before standing in *dotted* line.

From these results with the aid of the graphs, the following conclusions may be deduced:—

1. the degree of tarnishing is always specific with respect to a corresponding wave length, but
2. it shows some regularity in each system of the alloys;
3. with pure metals, the tendency of tarnishing is different from those of their alloys;
4. by comparing the values of the reflective powers of a sample, when polished and tarnished, for any wave length, the change of colour of a metallic surface may be determined.

The investigator wishes to express his thanks to Professor M. Chikashige for his valuable suggestions and kindly help throughout the course of this work.