United States Patent

Abbott

[15] **3,661,569**

[45] **May 9, 1972**

[54] **LOW ENERGY CONTACTS**

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[22] Filed: **June 19, 1969**

[21] Appl. No.: **834,796**

[52] **U.S. Cl.** ....**75/165,** 75/134 T, 75/151, 75/173 R, 200/166 C

[51] **Int. Cl.** **C22c 5/00**

[58] **Field of Search**......................75/165, 134 T, 151, 173 R; 200/166 C

[56] **References Cited**

UNITED STATES PATENTS

2,371,240	3/1945	Hensel et al.	75/165
2,400,003	5/1946	Hensel et al.	75/165 X

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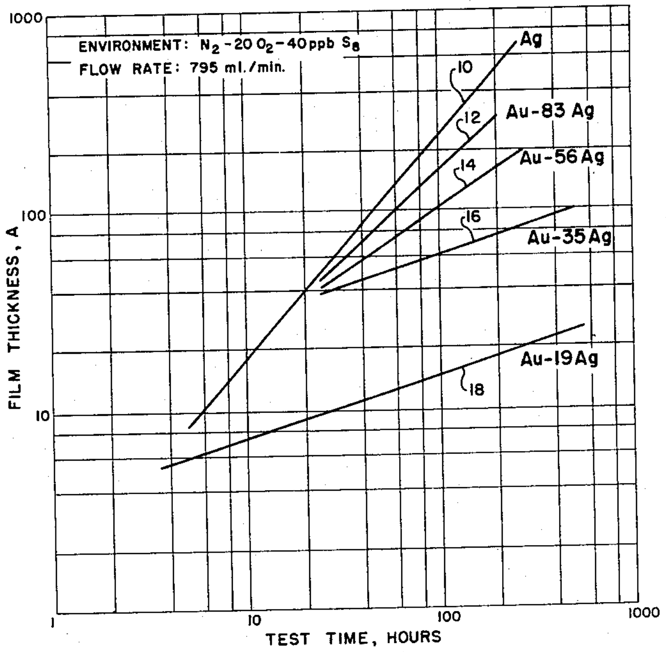
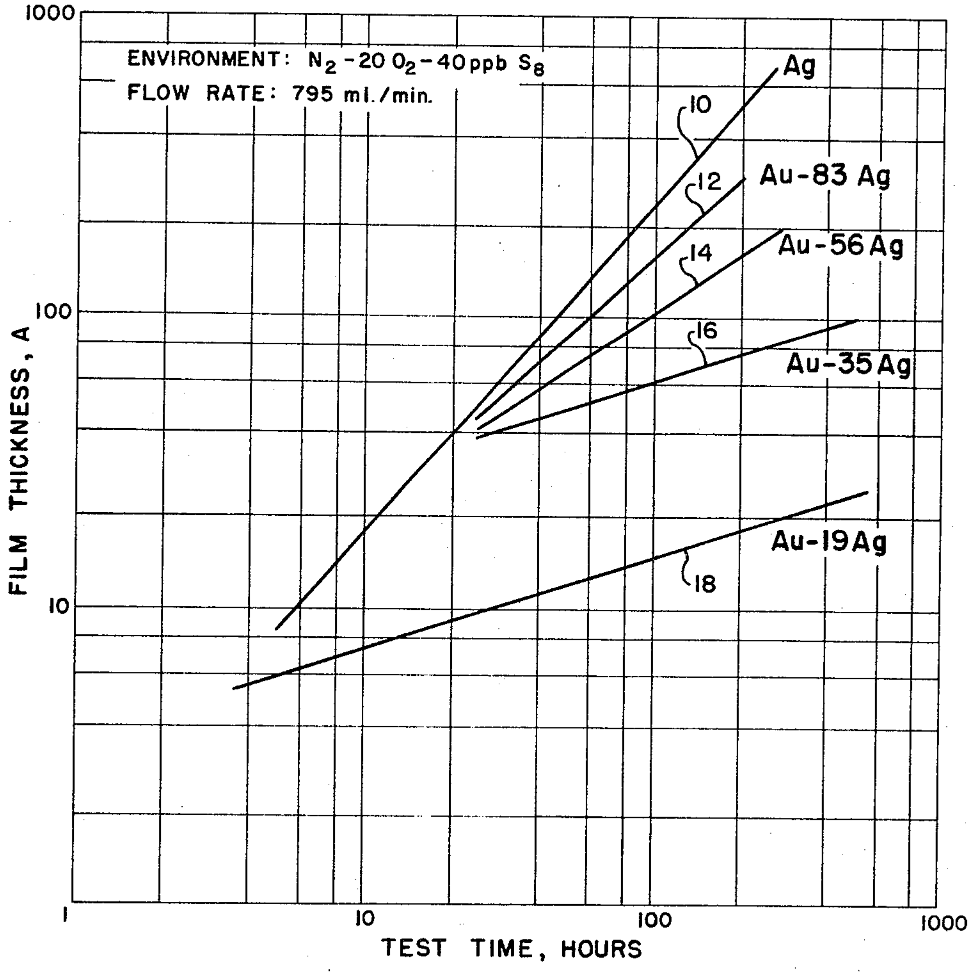
[57] **ABSTRACT**

High silver content (30 percent, by weight, or greater) gold base alloys are found to have exceptional resistance to silver sulfide tarnish when alloyed with from 0.25 to 10 percent, by weight, indium or preferably indium and cadmium each within the range of 0.25 to 10 percent and such alloys including those containing cadmium alone have been found to exhibit exceptional resistance to carbon film deposits in normal low energy switch applications and frictional polymer formation in sliding low energy applications.

7 Claims, 4 Drawing Figures

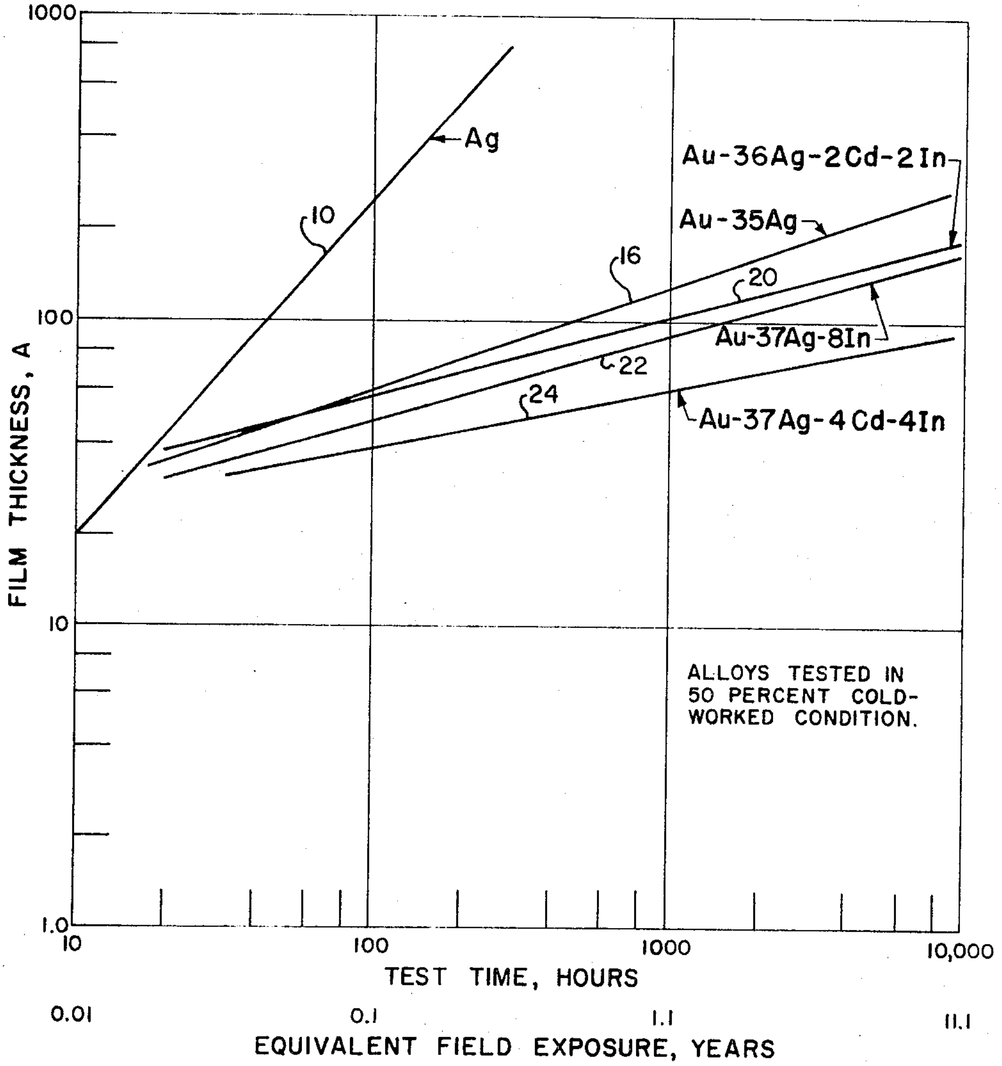


Tarnish Rates Of Au-Ag Alloys In Flowers Of Sulfur At 30° C



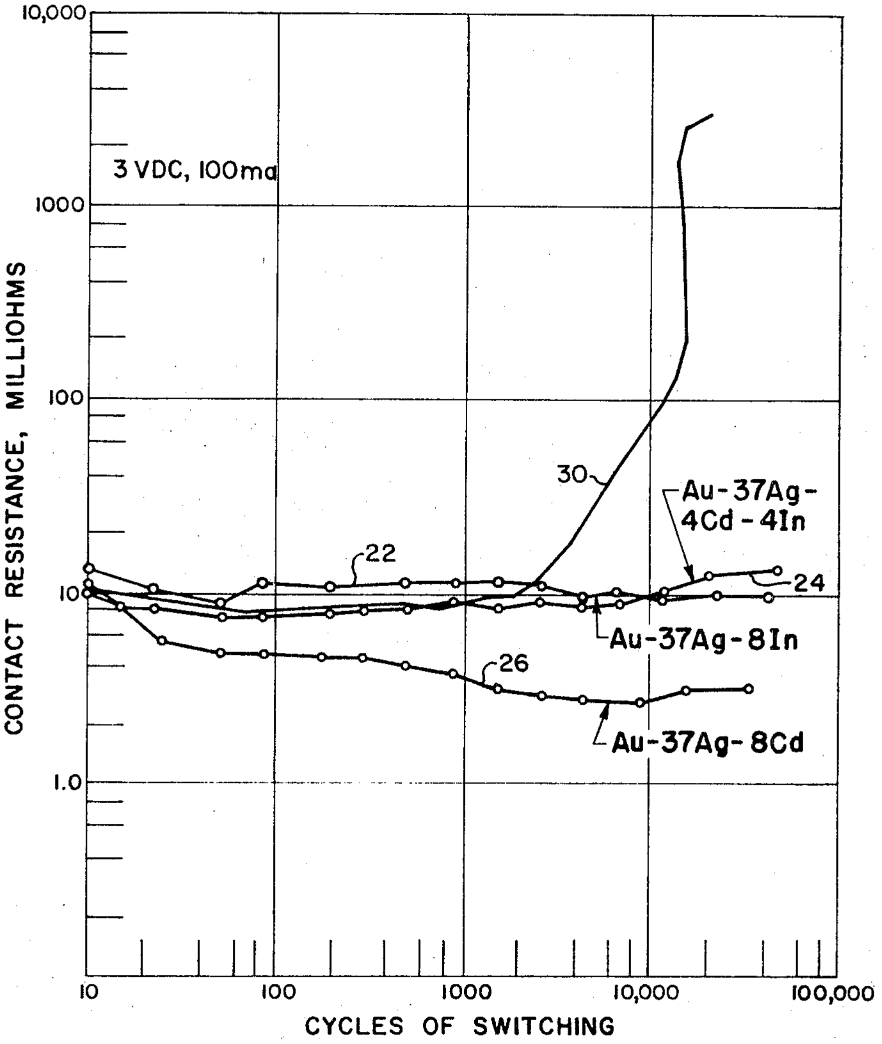
Tarnish Rates Of Au-Ag Alloys In Flowers Of Sulfur At 30° C

Fig. 1



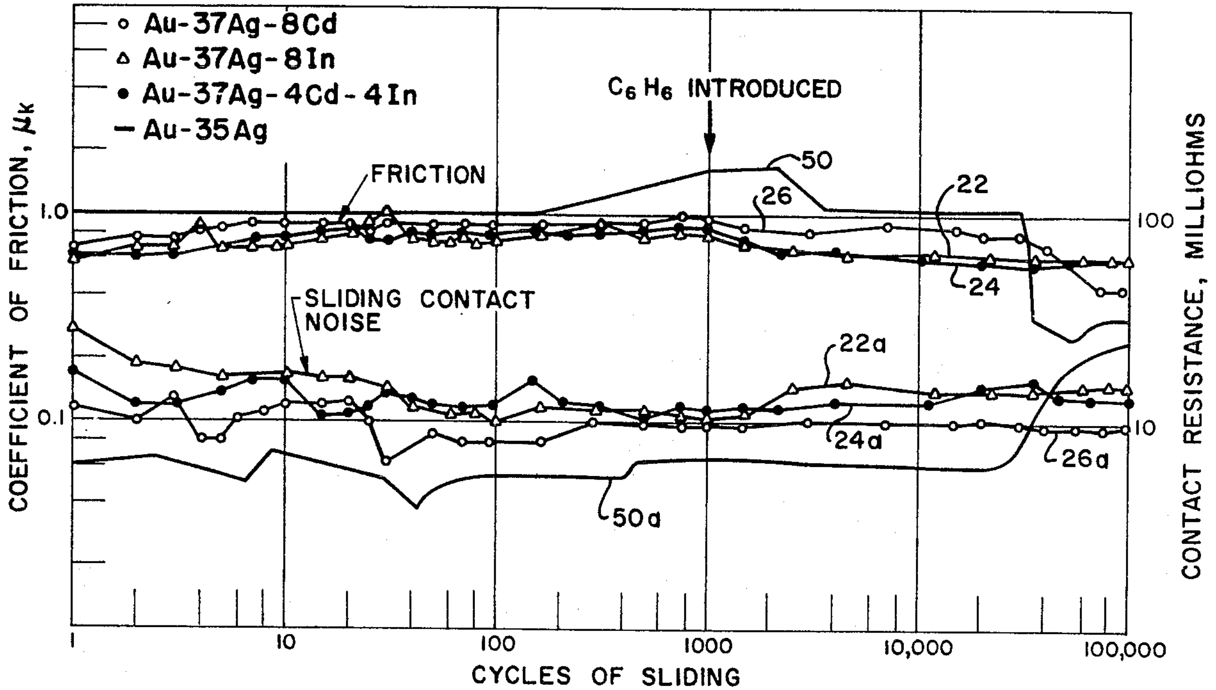
Tarnish Rates Of Au-Ag Alloys In Flowers Of Sulfur At 30° C

Fig. 2



Contact Resistance Of Au-Ag Alloy Relay Contacts In N_2-C_6H_6

Fig. 3



Sliding Contact Characteristics Of Au Alloys In N_2 And N_2-C_6H_6 Mixtures

Fig. 4

LOW ENERGY CONTACTS

BACKGROUND

This invention relates to improved electrical contact materials and relates in particular to a new and novel gold base alloy which exhibits improved characteristic of low energy electrical contact applications.

The metal terminal points of switching devices that are periodically brought together or separated to complete or interrupt electrical circuits are subjected to a wide variety of mechanical, electrical, and chemical environmental conditions that require a correspondingly wide variety of properties to effectively withstand such conditions. An ideal alloy for a particular application is one that does not erode, melt, or fuse in the presence of the electrical resistive and arc heat, provides low contact resistance between the contacting surfaces, does not form current inhibiting films (oxides, sulfides, polymers, carbon deposits, etc.), possesses sufficiently high hardness to provide wear resistance, is sufficiently ductile for fabrication, and is sufficiently low in cost to be feasible for the application.

Where high voltage and/or amperage circuits are involved, high melting point materials are generally required frequency at the sacrifice of other properties such as corrosion resistance. Where low-voltage, low-amperage applications are involved, such as microcircuits, telephone relay switches, etc., the most satisfactory alloys are the precious metal contact materials such as gold, silver, platinum, palladium, and alloys thereof. Such metals and their alloys possess relatively low melting points but where the potential is less than about 50 volts and current flow is less than about ½ amp., these materials may be successfully employed. Their chief value in such applications relates largely to their resistance to corrosion. Switching devices made of these materials are capable of long time reliability even in the presence of relatively corrosive environments. However, sticking, wear, erosion, and corrosion continue to be a problem.

One of the most significant metals for low-voltage low-amperage switching applications is gold and its alloys. Gold is unsurpassed in its resistance to oxidation and sulfidation but possesses a relatively low melting point, is susceptible to erosion and is costly. Also current retarding carbon and polymer deposits tend to form on the contacting surface of gold (and its alloys) when utilized as electrical contact points where organic vapors are present. Such vapors are generally present in switching devices of this type emanating from surrounding insulating materials, switch lubricating greases, etc.

Elemental gold is too soft for many electrical contact applications particularly where the switch application involves frequent opening and closing so that frictional wear is substantial. However, it is possible to make relatively small additions of alloying constituents such as silver to effect some hardening.

Silver possesses many qualities that surpass those of gold. For example, this metal has the highest electrical and thermal conductivity properties of any metal or alloy and is reasonably resistant to oxidation in air. Additionally, silver is in far greater supply than gold and consequently is far more economical to use. However, silver is particularly susceptible to sulfur attack forming sulfide films of a thickness that creates significant electrical contact resistance.

A frequently employed alloy for low energy (low-voltage low-amperage) switching applications consists of gold-silver alloys consisting of about 5–30 percent, by weight, silver balance essentially gold. The silver addition hardens the gold and reduces the overall costs. However, as the silver contents rise, the tarnish resistance of the alloy decreases, particularly as it relates to the formation of sulfides. At the lower silver contents, the alloy is susceptible to carbon and polymer deposits from organic vapor.

The elements indium and cadmium are known additions to gold for various purposes. For example, in the alloy of U.S. Pat No. 2,400,003, indium additions to gold alloys containing up to 24 percent silver are made to reduce the metal transfer tendency of these compositions. In the alloy of U.S. Pat. No. 2,806,113, the addition is made to reduce the formation of metal dust due to mechanical abrasion and the formation of burnished layers. In all of the compositions taught by these and other prior art publications, the recognized compositions contain less than 30 percent, by weight, silver. The reason for this, of course, is that compositions containing greater amounts of silver exhibit corrosion resistance and particularly resistance to the formation of sulfide films that is more like silver than gold while simultaneously exhibiting a susceptibility to carbon and polymer deposits.

THE INVENTION

I have now found that gold alloys having high silver content (i.e., 30 percent, by weight, or greater) exhibit unexpectedly high resistance to sulfide film formation when alloyed with from 0.25 to 10 percent, by weight, indium and particularly when further alloyed with from 0.25 to 10 percent, by weight, cadmium.

I have further discovered that these alloys including those containing cadmium alone (Au—30 percent or greater, Ag—10 percent Cd) are suprisingly resistant to the formation of current inhibiting carbon films during normal contact applications and polymer film formation during sliding contact applications.

Optimum results are experienced by making indium plus cadmium alloying additions to gold base alloys containing 30 to 60 percent, by weight, silver.

THE DRAWINGS

The unexpectedly high tarnish and carbon film-resistance properties of the alloy of the present invention are best illustrated by the data of the tables and the drawings wherein:

FIG. 1 is a graph showing the silver sulfide tarnish rates of binary gold-silver alloys;

FIG. 2 is a graph showing the silver sulfide tarnish rates of the electrical contact alloys of the present invention;

FIG. 3 is a graph showing the contact resistance of the present contact alloys as applied to normal switch applications and illustrates their resistance to carbon film formation; and

FIG. 4 is a graph showing the contact resistance and coefficient of friction of the present contact alloys as applied to sliding switch applications and illustrates their resistance to adverse polymer formation.

DETAILED DESCRIPTION

When silver is exposed to sulfur-containing atmospheres (free or elemental sulfur), a tarnish film of Ag_2S forms on its surface. This film grows in accordance with time and other environmental conditions (particularly the availability of free or elemental sulfur) until it constitutes an electrical current barrier. Where the sulfur content of the surrounding atmosphere is relatively constant, as when exposed to ordinary atmospheres, the film grows.

This film also forms on the surface of Au-Ag alloys. However, when low silver content, Au-Ag alloys, are exposed to free sulfur-containing atmosphere, the Ag_2S tarnish film forms at a slower rate than on pure silver and its growth rate depends on the silver content. Where the silver content of the alloy exceeds about 30 percent, by weight, the Ag_2S film grows at a rate equivalent to that of pure silver until an intermediate film thickness of from about 30 to 40 angstroms is reached whereupon a retarded growth rate occurs depending on the exact gold content. The combined tarnish film growth is sufficient to reduce the attractiveness of the alloy. Consequently, gold-base alloys containing more than about 30 percent, by weight, silver have not been extensively utilized in the past.

This phenomenon is best illustrated by the data of FIG. 1 of the drawings. The curves **10**, **12**, **14**, **16**, and **18** represents Ag_2S film thicknesses (in angstroms) of specimens of pure silver **10** and alloys of increasing gold (or decreasing silver) content (curves **12**, **14**, **16**, and **18**) after exposure to a sulfur-containing atmosphere (nitrogen—20 parts oxygen—40 parts per billion free sulfur).

These accelerated sulfur tarnish tests consists of positioning rod-shaped specimens (0.100 in. × 1.500 in.) in a glass reaction chamber (200 mm Scheibler desiccator) and introducing the specified gas flow through a glass tube extending downward (vertically) from the center of the chamber to within ½ inch of its bottom. The specimens are positioned symmetrically around the glass-inlet tube at a 45 degree angle and in a single layer. The distance from the center and bottom of the desiccator to the center of the rods were 7.5 and 10.0 centimeters, respectively. Testing was conducted at a temperature of 30° C. ± 0.5° C. The gas was purified prior to use by passage through a 1 × 18 inch molecular sieve column. The flow rate was 795 ± 10 ml/min. The gas base was N_2 —200_2 mixture to which sulfur vapor was added by saturating the mixture in temperature controlled columns. The sulfur vapor concentration was calculated and extrapolated from known data.

It will be noted that each of the curves of FIG. **1** (except curve **18**) intersect the curve **10** for pure silver at a definite Ag_2S thickness. These values are in the range of 25–40 A for the 35, 56, and 83 percent, by weight, Ag alloys (curves **16**, **14**, and **12**) and **5–6**A for the Au-19 Ag alloy. Thus, it is readily discernible that the overall tarnish processes of Au-Ag alloys involves: (1) an initial linear rate of tarnish that is equivalent to that of pure silver; and (2) a secondary or lower rate of film (Ag_2S) formation.

I have found that the addition of from 0.25 to 10 percent, by weight, of indium or indium plus 0.25 to 10.0, by weight, cadmium to the gold-silver alloys containing 30 percent or more silver, and particularly where the silver content is within the range of from 30 to to 50 percent, by weight, materially alters the secondary or lower rate of Ag_2S tarnish film formation.

This phenomenon is best illustrated by the data of FIG. **2**. Curves **10** and **16** of FIG. **2** are curves **10** and **16** of FIG. **1** showing the corrosion or tarnish film formation of Ag_2S of pure silver and Au—35 percent Ag alloy. Curves **20**, **22**, and **24** show the corrosion rate or tarnish film formation of gold-silver alloys containing greater than 30 percent, by weight, silver and varying indium contents within the range of 0.25 to 10 percent, by weight, as set forth in Table I below:

TABLE I. Tarnish Characteristics of Au-Ag Alloys

Curve[c]	Alloy Wt. %	At. %	Transition Film Thickness[a] A	Rate Exponent[a] n
18	Au-19Ag	Au-30Ag	6	**3**
16	Au-34.5Ag	Au-50Ag	32	**3**
–	Au-36.4Ag-3.80Cd	Au-50Ag-5Cd	40	**3**
–	Au-36.4Ag-3.87In	Au-50Ag-5In	35	**>5**[b]
26	Au-37.5Ag-7.80Cd	Au-50Ag-10Cd	35	**3.01**
22	Au-37.5Ag-7.93In	Au- 50Ag-10In	27	**3.62**
20	Au-36.4Ag-1.89Cd-1.93In	Au-50Ag-2.5Cd-2.5In	37	**3.85**
24	Au-37.5Ag-3.89Cd-3.95In	Au-50Ag-5.0Cd-5.0In	25	**5.18**

(a) 50 percent cold-worked condition.

(b) Tested to only 120 hours.

(c) Compositions estimated in drawings.

The data of Table I and FIG. **2** show conclusively that indium, and particularly the combination of cadmium plus indium additions, significantly decreases the tarnish rate of the Au—30 percent, by weight, or more Ag alloys. The table and graph show that the rate decrease is generally attributable to decreases in the secondary corrosion rates. For example, curve **16** shows a transition thickness of 32 A and a corrosion rate exponent (n) of 3 for Ag—34.5 Ag alloy while substantially the same alloy containing 3.87 percent, by weight, In exhibits a similar transition film thickness (35A) but a much higher rate exponent (over 5).

The rate exponent relates to the secondary tarnish rate as follows:

$X^n = kt$ X>X transition

where

X = film thickness, A

t = time, hours

n = rate exponent 1

k = constant

Thus, the larger the exponent n the smaller the film thickness X for any given period of time t. For binary Au-Ag alloys containing up to 35 weight percent silver, values of $n = 3$ were obtained indicating that the secondary stage of tarnishing followed a cubic rate equation. Silver contents above 35 percent, give progressively lower values of n eventually reaching $n =$ for pure silver. Consequently, the curves **20**, **22**, and **24** of FIG. **2** and the data of Table I show that the addition of indium and indium plus cadmium materially increase the exponent indicating a significantly slower secondary tarnish rate.

Carbon deposits on the surface of electrical contacts are related to the presence of organic vapors and electrical arcing during opening and closing of electrical switches commonly referred to as "make and break "type contacts. This problem is not related to sliding and may occur where only normal contact loading is involved. Accordingly, the alloys of the present invention were tested in a controlled environment utilizing two 0.10 inch diameter × 1.0 inch long rod-shaped specimens as electrical contact points. These rods were crossed (90°) in a horizontal position—one being in a fixed position and the other being vertically positionable to effect normal make and break contacts with the fixed rod. When the rods were in contact with one another, a contact force of about 2.5 grams was maintained. The make-and-break cycle rate was one complete cycle every two seconds (1.1 seconds closed and mated and 0.9 seconds open).

The organic vapors commonly present during switching operations are the solvents from the resinous insulating materials. Such solvents are often aromatic compounds such as benzene. Consequently, the controlled environment of the present tests consisted of a nitrogen-benzene mixture (N_2—560 ppm C_6H_6, 250 cc/min at 760 mm Hg).

When carbon deposits occur on the surface of make-and-break contacts, the contact resistance rises sharply. This phenomenon or the point of carbon formation is referred to as activation since arcing increases (and consequently an even greater carbon deposit occurs). Curve **30** of the graph of FIG. **3** illustrates "activation" or excessive carbon formation on binary Au-Ag alloys containing up to about 60 weight percent silver exposed to the aforementioned make-and-break testing at 3 volts direct current and 100 milliamperes during about 50,000 cycles of switching. The alloys of the present invention (curves **22**, **24**, and **26** representing Au-37Ag-8In, Au-37Ag-4Cd-4In, and Au-37Ag-8Cd, respectively, resisted activation for over 50,000 cycles. The Au-37Ag-8In gave the most stable contact resistance-life characteristics of 7 to 10 milliohms. A relatively large resistance decrease was obtained for the Au-37Ag-7.8Cd alloy during the first 1,000 cycles of switching after which the resistance remained stable (3–3.5 milliohms). Although higher values (10–13 milliohms) were reached by the Au-37Ag-4Cd-4In alloy these values are exceptionally good for a gold-base alloy.

Photomicrographic examination of the contact areas of the Au-37Ag-8Cd and Au-37Ag-8In alloys after 40,000 cycles showed no evidence of organic contamination.

Thus, it is apparent from the data of FIG. **3** that the alloys of the present invention in addition to unusual sulfide tarnish resistance are resistant to "activation" or carbon film formation in low energy applications.

A still further advantageous feature of the present alloys relates to their unusual resistance to frictional polymer formation in sliding contact applications. Such polymers are known to form where organic vapors are present and the contact is made in a manner where frictional heat is generated such as in slip ring electrical contacts. The phenomenon is independent of arcing and will form independently of an actual electric current.

Testing designed to simulate average field applications involved crossing 0.1 inch diameter × 1.5 inch test rods at 90° as described above. However, instead of make-and-break cycles one rod was caused to slide over the surface of the other in violin fashion (at a constant reciprocal velocity over a 1 cm length wear tract). The fixed rod (called the rider) was actually horizontally movable with the reciprocating rod but offered predetermined resistance. The actual distance the rider moved horizontally was translated into coefficient of friction values. A cycle was completed every two seconds (1 cm/sec.). The contact (or normal) force was maintained constant for all tests. The specimens exhibited substantially uniform surfaces (a profilometer reading of about 20 microinches R.M.S.).

Although polymer formation is generally regarded to be undesirable, the exact type of polymer that forms an electrical contact varies in accordance with the material from which the contact is constructed and the organic vapor that is present. Some such films actually act as lubricants decreasing friction without materially changing contact resistance (noise). However, many drastically increase noise. Curve **50** and **50***a* of the data of FIG. **4** shows the coefficient of fraction and contact resistance values, respectively for Au-37Ag alloy. The drop in coefficient of friction of about 50,000 cycles is attributable to the lubricating qualities of the polymer. This drop in coefficient is accompanied by a sharp increase in noise.

Curves **22**, **24**, and **26**; **22***a*, **24***a*, and **26***a* relate to Au-37Ag-8In, Au-37Ag-4Cd-4In, and Au-37Ag-8Cd compositions, respectively. These data show excellent contact-resistance stability and low friction in both nitrogen and N_2-C_6H_6 environments (nitrogen gas containing benzene vapor). Polymer formation occurred only on the Au-37Ag-7.8Cd alloy (curve **52**) and this polymer was of a type that lubricated the contacting surfaces to give even lower friction values ($\mu_k = 0.44$) without raising contact resistance.

What is claimed is:

1. An alloy consisting of from 30 to 60 percent, by weight, silver, 0.25 to 10 percent, by weight, of at least one element selected from the group of cadmium and indium, balance essentially gold.

2. The alloy of claim **1** wherein both cadmium and indium are present, each within the range of 0.25 to 10 percent, by weight.

3. A gold-base alloy consisting of from 30 to 60 percent, by weight, silver, from 0.25 to 10 percent, by weight, indium, balance essentially gold.

4. An electrical contact formed of an alloy that consists essentially of from 30 to 60 percent, by weight, silver, 0.25 to 10 percent, by weight, of at least one element selected from the group cadmium and indium, balance gold, said contact having the properties of high resistance to carbon film build up on contacting surfaces in normal low energy applications and high resistance to frictional polymer formation in low energy applications.

5. The contact of claim **4** wherein the alloy contains both cadmium and indium each within a range of from 0.25 to 10 percent, by weight.

6. The contact of claim **4** wherein the alloy contains indium and has the property of a high resistance to silver sulfide tarnish.

7. The contact of claim **4** wherein the alloy contains indium plus cadmium and has the property of a high resistance to silver sulfide tarnish.

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