Patented June 29, 1954

2,682,593

UNITED STATES PATENT OFFICE

2,682,593

ELECTRICAL CONTACT

Alfred L. Jenny, Pittsfield, Mass., assignor to General Electric Company, a corporation of New York

No Drawing. Application June 28, 1949, Serial No. 101,910

4 Claims. (Cl. 200—166)

1

The present invention relates to an electrical contact. It is more particularly concerned with a switch contact which is resistant to corrosion by sulfur when immersed in oil and to a method of making such contact.

Silver is one of the most widely used metals for electrical contact purposes. However, silver contacts are not wholly satisfactory for oil immersed switching apparatus due to the formation of silver sulfide scale on the exposed or non-engaging areas of the contact surface. As this sulfide is a good conductor of electricity, it is likely to cause electrical failures when it drops off the contact surface and collects on insulated or other parts of the oil immersed switch or other electrical equipment. It is important, therefore, to prevent sulfide formation on all parts of solid silver or silver plate applied for contact purposes and a primary object of the present invention is to provide such an electrical contact which is resistant to corrosion by sulfur.

Briefly described, the electrical contact of the present invention comprises a silver-rich silver amalgam, the exposed surfaces of which are composed of silver iodide and mercury iodide.

Any suitable metal can be employed as the base or backing material for the contact. Copper is ordinarily employed because of its high conductivity and low cost. However, silver or alloys of copper and silver can be used if desired, the only requirement being that the exposed surface of the electrical contact be composed of a layer of silver amalgam, that is, a silver-mercury alloy, preferably containing from about 5 to 25 percent mercury.

As copper is the most commonly used conductor, the invention will be particularly described with reference to a switch contact comprising a copper base or backing. Employing such a base, the copper part is first provided with a coating of silver. The silver suitably may be applied by electroplating employing any suitable silver plating bath and allowing the part to remain in the bath until a silver layer of the desired thickness, usually from about ½ to 5 mils, has been obtained.

The surface layer of silver is next alloyed with mercury to provide a silver amalgam layer of about the same thickness containing from 5 to 25 percent by weight of mercury. The mercury preferably is applied by plating onto the silver surfaced part in order to obtain a uniform distribution of the mercury and is thereafter caused to diffuse into and alloy with the silver. Alternatively, the silver-mercury layer may be formed

2

by codeposition of silver and mercury on the metal base.

The invention is not limited to the use of any particular mercury plating bath. The mercury is electro-deposited on the silver surface in an amount sufficient to provide a silver-amalgam layer of the desired composition. When first plated, the mercury surface has a high lustre with the characteristic appearance of mercury. To obtain the alloy formation the mercury plated part is aged at room or elevated temperature during which time the lustre disappears and is replaced by a dull, matte surface not unlike the original silver surface. The required amount of diffusion is usually accomplished by immersion of the part in boiling water for from 2 to 30 minutes, generally about 15 minutes. Aging at room temperature for about one week produces about the same degree of alloying as 15 minutes at 100° C.

When the proper silver-mercury layer has been developed, the surface thereof is passivated by a suitable treatment designed to convert the silver and mercury at the surface to the corresponding iodides. Although the silver amalgam in itself is more resistant to sulfiding than silver alone, after long periods of time the mercury gradually diffuses through the entire piece leaving practically free silver on the surface. The immediate formation of an iodide film in accordance with the present invention captures the proper amounts of silver and mercury on the surface as iodides, passivating the surface, and removing any concern about the subsequent loss of the remaining mercury by further diffusion.

For maximum resistance to sulfiding, an amalgam layer having a nominal analysis of 90 percent silver and 10 percent mercury obtained by diffusion for about 15 minutes at 100° C. is preferred. In all cases, the amalgam coated part should be treated to form the desired iodized surface within a reasonable time after the requisite amalgam layer has been prepared. The iodization is preferably accomplished anodically in a suitable alkali metal iodide solution such as a 10 percent solution of potassium iodide having a pH of about 10. As it is desired to convert as much of the mercury as possible to mercurous iodide, the anodic treatment should be carried out at a current density less than 15 amperes per square foot and preferably less than 10 amperes per square foot with the time of treatment being such that the mercury iodide comprises at least 5 percent of the metal iodide content of the surface film. It has been found that the

ratio of HgI to AgI in the film varies inversely as the current density and time of treatment. While this ratio also varies directly as the mercury content of the amalgam, it is usually higher than the Hg/Ag ratio of the alloy particularly at low current densities and short treating times and films having very good sulfide resistance have been obtained containing as high as 80–85% HgI, balance substantially AgI.

The effect of time and current density on the composition of the iodide film are shown by the results of a series of tests in which copper contacts surfaced with a layer of 90 percent silver—10 percent mercury obtained by diffusion for 15 minutes in boiling water were anodically treated in a 10 percent potassium iodide solution as indicated in Table I.

TABLE I

Sample	Treatment (min.)	Anodic Cur. Dens. (Amps./sq. ft.)
1 and 2	5	4.6
3 and 4	7.5	4.6
5 and 6	10	4.6
7 and 8	3	6.9
9 and 10	6	6.9
11 and 12	9	6.9
13	2	9.2
14	2	7.6
15	4	15.2
16	3.25	18.6
17 and 18	5	9.2

Each sample contact was weighed after treatment to determine iodine pickup and the film weight determined by rapid solution in sodium cyanide. The composition of the films, i. e., the relative proportion of silver iodide and mercurous iodide was calculated by dividing the film weight by the iodine pickup to obtain a factor. This factor for pure silver iodide is

$$\frac{AgI}{I}$$

or 1.85 and for pure mercurous iodide is

$$\frac{HgI}{I}$$

or 2.58. On the proper assumption that the films contain only iodides, any mixture of silver and mercury iodide has a factor between the two above, and is indicative of film composition by the inverse lever law.

The composition of the iodide films obtained on the above-described samples are set forth in Table II.

TABLE II

Samples	Milligrams I pickup	Film Wt.	Factor	Percent AgI	Percent HgI	mgms. HgI formed
1 and 2	29.85	62.85	2.1	65	35	22.0
3 and 4	48.85	98.8	2.02	77	23	22.8
5 and 6	68.85	136	1.975	83	17	23.0
7 and 8	31.05	61.25	1.975	83	17	10.5
9 and 10	65.7	126.1	1.92	90.5	9.5	12.1
11 and 12	103.6	197.	1.90	93	7.0	13.8
13	30	58.6	1.95	86	14	8.2
14	23.2	49.4	2.12	63	37	18.2
15 and 16	123	220	1.79	100	0.0	0.0
17 and 18	68.7	130.5	1.9	93	7	9

From the data of Tables I and II, it is apparent that the composition of the iodide film is a function of (*a*) the current density and (*b*) the time of treatment and can be controlled by current density or time of treatment or both. The results obtained with samples 15 and 16 show that no HgI can be obtained at current densities of 15 amperes per square foot or higher even when the silver amalgam surface contains a substantial amount of mercury.

The high resistance to sulfide formation of two iodized silver amalgams as compared with an untreated silver surface and an iodized silver surface and the desirability of having an iodide film comparatively rich in mercurous iodide is shown by a series of tests on sample contacts treated as shown in Table III.

TABLE III

Sample No.	Alloy	Diffusion (100° C.)	KI Treatment		Film Composition
			Amp.	Min.	
1 and 2	100% Ag	None			Ag_2S.
3	90 Ag, 10 Hg	15 min	0.1	4	65—AgI. 35—HgI.
4					
5	90 Ag, 10 Hg	do	0.15	9	93—AgI. 7—HgI.
6					
7 and 8	100% Ag	None	0.1	2	AgI.

Samples 1 and 2 were pure silver blanks, 3 and 4 were treated to have a relatively HgI rich film, 5 and 6 were treated to have a relatively AgI rich film, and 7 and 8 were 100% AgI films. Each sample was exposed to 125 cc. of oil containing 30 milligrams available sulfur (.03% S), and the test continued for 980 hours at 60° C. After 500 hours, portions of the silver sulfide growing on the surface of the AgI film (7 and 8) were dislodged in degreasing, handling and weighing these samples so the further tests on these samples were meaningless. The increase in weight of the various sample contacts as a result of sulfide formation that is the weight of sulfur picked up out of a total of 30 mg. available sulfur, are given in Table IV.

TABLE IV

Sulfur pickup (mg.) after exposure time (hours)

Samples	90 hrs.	134 hrs.	452 hrs.	641 hrs.	980 hrs.
1 and 2 (ave.) mg.	28.4	28.8	29.3	29.3	29.3
3 and 4 mg.	0.0	0.0	0.25	1.6	10.0
5 and 6 mg.	0.85	3.0	3.80	3.75	12.6
7 and 8 mg.	1.45	2.85	24.2	15.20	14.8

From these results it is seen that the iodide films on the silver mercury alloys afford excellent protection against sulfiding types of corrosion even under the highly accelerated conditions of the test. It is also evident that the best protection is noted with the iodide films comparatively rich in mercurous iodide so that accordingly, it is desirable to employ contacts in which the iodide films comprise at least 15 percent mercurous iodide.

The contact resistances of the iodide coated silver-amalgam contacts are comparatively low as shown by the following test results on various oil-immersed cooperating ½ in. rounded contacts operating at 80° C. and 20 pound contact pressure and a current of 100 amperes A. C.

TABLE V

	Resistance in Microhms		
	Start	After 1 Week	After 13 Weeks
Silver to Silver	39.5	39	32
Silver-mercury to Silver-mercury	34	33	150
Silver Iodide to Silver iodide	200	150	85
Silver-mercury iodide to silver-mercury iodide	390	230	82

As compared with the straight silver iodide coated contacts, the contacts of the present invention have surfaces which are much less porous or more dense probably due to the mercury impregnating the silver surface or to the mercury iodide formed upon iodization.

While the invention has been specifically described with reference to the use of a potassium iodide solution for forming the iodide surface film, it is of course not limited thereto. For example, any suitable iodide such as a solution of sodium iodide may be substituted for the potassium iodide. Alternatively, while a longer exposure time will be required, satisfactory iodide films rich in HgI can also be formed merely by immersion of the silver amalgam contact in a solution of iodine, for example, in carbon tetrachloride.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A switch contact comprising a high conductivity metal base, and a coating of a silver-rich silver-mercury alloy containing from 5 to 25 per cent mercury the surface of which is composed of silver and mercury iodide, the mercury iodide comprising at least 5 percent by weight of the combined iodide components of the surface.

2. An oil-immersed switch contact having a coating of silver containing from 5 to 25 percent mercury, the silver and mercury at the surface of said coating being substantially in the form of silver iodide and mercury iodide.

3. An oil-immersed switch contact having a coating of a silver amalgam containing about 10 percent mercury, the surface of said coating comprising essentially silver iodide and mercury iodide with the mercury iodide comprising about 35 percent of the iodide content of the surface.

4. The method of making an electrical contact resistant to corrosion by sulfur which comprises providing a copper base with a layer of silver having a thickness of from about ½ to 5 mils, electroplating a layer of mercury on the silver layer such that on diffusion of the mercury into the silver layer there is obtained a silver-mercury layer containing about 10 percent mercury, making the resultant product the anode in a dilute aqueous solution of an alkali metal iodide and passing current through said solution and anode of a current density less than 10 amps./sq. ft. for a time sufficient to form on the surface of the silver-mercury layer a film comprising silver iodide and mercury iodide in which the mercurous iodide comprises from 5 to 85 percent of the total amount of iodides in said film.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
26,978	Edwards	Jan. 31, 1860
1,602,595	Sheppard et al.	Oct. 12, 1926
1,720,216	Gray et al.	July 9, 1926
1,758,293	Murray	May 13, 1930
1,860,505	Jones	May 31, 1932
2,116,215	Ruben	May 3, 1938
2,195,231	Weder	Mar. 26, 1940
2,281,446	Laise	Apr. 28, 1942
2,430,468	Julich et al.	Nov. 11, 1947
2,469,878	Hannon et al.	May 10, 1949
2,583,581	Lukens	Jan. 29, 1952

OTHER REFERENCES

"Silver in Industry," by Addicks (1940), page 310.