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(54) SILVER ALLOYS OF HIGH SULPHURATION RESISTANCE

(71) We, KABUSHIKI KAISHI SUWA SEIKOSHA, a Japanese company, of 3-4, 4-chome, Ginza, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to silver alloys of high sulphuration resistance, and to products made of such alloys.

As is well-known, silver alloys have been used for ornaments and for industrially made art products such as rings or silver table-ware or watch cases or dentistry applications, and in all these applications the bright white colour and soft colour tone of the silver has been highly prized. However, silverware has the defect that it reacts with sulphur compounds contained in air, or in the case of watch cases, in natural perspiration, and as a result black silver sulphide is in time produced to cause discoloration.

In order to overcome this defect it is known to make silver alloys containing palladium and gold, for instance in dentistry use. Certainly these alloys are improved as regards their sulphuration resistance, but the natural colour of silver is lost and becomes tinged with grey and moreover these alloys are extremely expensive. In a larger scale industrial use a common expedient has been to plate silver with rhodium for surface protection, but while such plating is quite effective against sulphuration, the natural colour of silver can no longer be seen.

The present invention seeks to eliminate

the above defects and to provide silver alloys which will remain in their natural silver white colour, will not become black or otherwise discoloured due to sulphuration and which in expense do not exceed the price of silver or actually are cheaper than silver.

According to one aspect of the present invention, there is provided a silver alloy of high sulphuration resistance having the following percentage composition by weight:

Sn	4 —10%
In	0.5—12%
Zn	0.1— 5%
Ag	balance.

All references to percentages throughout this specification and claims are by weight.

Preferably the alloy set forth above contains additionally any one or more of the metals Ti, Be, Z, Cr and Si in an amount 0.001—1%, Sb, Al and Ge in an amount 0.001—5% in total.

Additionally or alternatively, the alloy may contain copper in an amount 0.001—10%.

According to another aspect of the present invention there is provided a silver alloy having the following percentage composition by weight:

Sn	4 —10%
In	0.5—12%
Ag	balance.

As will be seen from the foregoing, silver alloys of high sulphuration resistance have

been obtained by the addition of tin to silver which increases the sulphuration resistance and the mechanical strength of the alloy, and the effect is enhanced by the simultaneous addition of indium which together with tin very considerably improves sulphuration resistance. According to one aspect of the invention, the further addition of zinc to the alloy containing silver, tin and indium gives the best results for obtaining a silver alloy of high sulphuration resistance and good mechanical strength.

The effect of each additional element of the alloys according to the invention, and the reasons for restricting the ranges of these elements as set forth above, will now be described.

Tin is added because it oxidizes preferentially to silver. The tin oxide is stable and protects the surface of the alloy so as to prevent the formation of silver sulphide. The minimum amount at which the desirable effect on the sulphuration resistance begins to show has been found to be about 4% by weight, and as the amount of tin is increased the effect on the sulphuration resistance as well as on the mechanical strength increases. However, if the amount of tin exceeds 10% the colour of the silver proper is found to be discoloured to a less desirable grey hue. Moreover, such silver alloys become brittle and working such as drawing and rolling becomes more difficult. Accordingly, the range of tin is limited to 4 to 10% by weight.

Indium is very soluble in silver but has poor corrosion resistance. It has been found that if indium is added alone to silver in an amount exceeding 10%, the sulphuration resistance is not improved very greatly. However, the effectiveness of indium is much increased, as regards sulphuration resistance of silver, if it is added together with tin, with the result that the vivid colour of pure silver which had become tinged with grey by the addition of tin will be restored.

If a large amount of tin is added, addition of 0.5% indium shows a favourable effect on the sulphuration resistance and this effect is increased as the amount of indium is increased. However, it has been found that if the additional amount of indium exceeds 12%, the resulting alloys become tinged with yellow and their malleability is decreased. Accordingly, the top limit of indium has been fixed at 12%.

Zinc has a de-oxidizing effect on the alloys when they are melted. Generally, zinc exhibits a favourable corrosion resistance in air as well as in solutions containing salts, such as natural perspiration. Even with a comparatively small amount of zinc, its de-oxidizing effect is very marked. However, to obtain good corrosion resistance as well as good sulphuration resistance, it has been found that at least 0.01% of zinc is needed, while on the other hand if the amount of zinc exceeds 5%, the result-

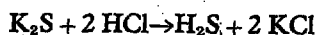
ing alloys become tinged with grey and also become brittle with the consequential deleterious effect on their malleability and ductility. Accordingly, where used, the range of zinc most suitable for the purposes of this invention has been found to be from 0.1 to 5%.

From the foregoing discussion, it will be understood that the favourable properties of pure silver can be maintained by the alloys of the present invention, and the largest single disadvantage of using pure silver, namely the black discoloration due to sulphuration, can be prevented by adding certain ingredients the prices of which are approximately the same as, or lower than, that of silver. Furthermore, the addition of tin and indium to the silver permits the mechanical strength of the alloys to increase greatly to enable the alloys according to the present invention to be used not only for ornaments and technical products but also for various industrial uses.

The present invention will be described in greater detail with reference to the following specific Examples.

EXAMPLE 1

Alloy No. 1 in accordance with the first aspect of the present invention having the composition of Sn 8.2%, In 2.1%, Zn 1.2%, balance silver, was melted and founded. The resulting alloy was subjected to repeated heat treatment and rolling processes whereafter it was formed into plates of 2 mm thickness. A test piece of 30 mm x 30 mm was cut off from the plate, was mirror polished by emery paper and a buff polishing machine, washed to remove oils and fats and kept in a sealed container into which 100 cc of 6N hydrochloric acid and 200 cc 2N potassium sulphide were poured and hydrogen sulphide gas was generated as follows:—



After keeping the test piece in the hydrogen sulphide gas for six hours, the test pieces was removed and examined for discoloration.

The examination showed that substantially no discoloration could be observed and the initial surface lustre and tone were well maintained.

For the sake of comparison, three further alloys were made, one comprising Sn of 8.9% with the balance silver, i.e. tin added singly; another alloy comprising In 9.7% and the balance silver, i.e. indium added singly; and a third alloy comprising Sn 8.7%, In 4.7% and the balance silver. These three alloys were respectively melted and founded and tested in the same way as the alloy No. 1 in accordance with the present invention.

As a result of the examination, it was found that the alloy containing tin only and the alloy containing indium only were discoloured respectively within five minutes while the surface

of the alloy including both tin and indium mixed together began to discolour to a light brown colour after some six hours.

From the above experiment, it was found that the sulphuration resistance of silver is best achieved by the synergistic effect of adding tin, indium and zinc all together.

It was also found that the alloy including tin only showed a white grey colour tone,

the alloy including indium single showed a silver colour tinged with light yellow but the alloy No. 1 according to the present invention maintains the soft silver white tone of pure silver.

EXAMPLE 2

Table 1 shows the compositions of various silver alloys according to the present invention and also three conventional silver alloys.

Alloy No. according to the invention	Sn	In	Zn	Ag
Alloy No. 2	5.2%	2.2%	0.4%	remainder
" 3	4.4	10.5	0.8	"
" 4	9.2	9.6	2.2	"
" 5	7.9	4.3	1.2	"
" 6	7.8	0.9	4.1	"
" 7	8.4	0.6	3.1	"
" 8	5.7	7.2	1.3	"
" 9	6.2	3.1	0.9	"
" 10	8.2	1.9	3.3	"
" 11	8.1	2.6	1.0	"
Pure silver	—	—	—	99.9% up
Sterling silver	—	—	—	92.5% (Cu 7.5%)
Au—Pd—alloy	—	—	—	70% (Pd 25% Au 5%)

TABLE 1

The melting process of the alloy according to present invention can be conducted also by using a carbon crucible in the same manner as that of conventional silver alloys. But it is desirable to add Zn before founding into ingot in order to fully display its deoxidizing effect. It is especially desirable to reduce the amount of oxygen absorbed under high temperature.

The conventionally used phosphoric fluxes etc. as deoxidizing agents have an extremely deleterious effect on the sulphuration resistance in the alloys according to the present invention. So they must not be used. Similarly S must be also prevented from being mixed in by accident at the melting stage. The founding is carried out by a metal mould. After face

scraping, the alloys are subjected to hot or cold rolling. The workability is very high. The heat treatment during processing is between 500°C and 650°C. As for the cooling method, a quick cooling is more effective than a slow one from the point of view of workability and sulphuration resistance.

The alloys shown in the example were produced in the same manner as mentioned above. The final reduction rate was 30% (cold rolling) and the alloys were formed into the plates having a thickness of 2 mm. Then test pieces were cut off from them respectively to examine their properties. The result is shown in Table 2.

Alloy No. according to the invention	Sulphuration resistance		Hv after 30% cold rolling	Colour tone
	gaseous H ₂ S	artificial sweat		
Alloy No. 2	○	○	118	silver white
" 3	○	⊙	147	semi-yellow and white
" 4	⊙	⊙	165	silver white
" 5	⊙	⊙	155	"
" 6	⊙	⊙	148	"
" 7	⊙	⊙	148	"
" 8	⊙	⊙	152	"
" 9	⊙	⊙	153	"
" 10	⊙	⊙	165	"
" 11	⊙	⊙	142	"
Pure silver	×	×	77	pure silver
Sterling silver	×	×	98	semi-yellow and white
Au—Pd—alloy	○	⊙	142	grey

TABLE 2

In testing the alloys for their sulphuration resistance, they were subjected to the same test of immersion in hydrogen sulphide gas as described above in Example 1, with the surface condition of the test pieces being examined after six hours. The result is indicated in Table 2 by the following code, namely a sign of two concentric circles denotes "no discoloration", the sign of a single circle shows "a little discoloration", and the sign of X shows "discoloration to black". It was found that the pure silver and the sterling silver discoloured to black within five minutes.

Another sulphuration resistance was carried out by immersing the test pieces in artificial perspiration, that is to say perspiration made up artificially to approximate the composition of the average human perspiration. The test pieces were kept in this composition at 36°C for 48 hours and thereafter examined. The result is also shown in Table 2 with the signs having the same meaning as before.

The composition of the artificial perspiration is given below and is thought to be substantially identical with that of the normal perspiration of a man.

NaCl	0.648~0.987%
Na ₂ S	0.006~0.025%
(NH ₂) ₂ CO	0.086~0.173%
NH ₄ OH	0.010~0.018%
Saccharose	0.006~0.022%
Lactic acid	0.034~0.107%
H ₂ O	Remainder

As Table 2 shows, the silver alloys according to the present invention exhibit high sulphuration resistance.

Next the alloys were also tested for hardness, and it was found that the alloys according to the present invention shows a hardness as shown in Table 2. From this it can be seen that the alloys according to the present invention have approximately the same mechanical strength properties as commercial brasses.

Further experiments were performed in an attempt to increase the mechanical strength and sulphuration resistance of the alloys according to the present invention, and it was found that this can be achieved by minimizing the size of crystal grains and making the quality substantially uniform by adding a very small amount of further additional elements, herein-

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after referred to as "sub-additional elements", taken singly or in any combination from the group comprising Ti, Zr, Be, Cr, Si, Al, Ge and Sb. These sub-additional elements are
5 thought to act in such a way as to make the silver atom stable and to protect the surfaces of the alloys by preferential oxidizing. It will be noted that all of these sub-additional elements have very stable oxides. Thus it is
10 thought that the sulphuration resistance is further increased by alloys incorporating one or more of these constituents by the formation of an oxide film to protect the surface of the silver alloy.
15 The addition of these further constituents allows the alloys to be heated to between 100 to 300°C in an atmosphere where oxygen is moderately rare, or in vacuo to make a stronger oxidized film than could be made at room
20 temperature. However, in doing this it is important to select the conditions, such as atmosphere and temperature, in such a way as to prevent the alloys from losing their lustre due to the oxide film. It has been found that
25 if the additional amount of these sub-additional elements is less than 0.001%, the above-described favourable effect cannot be obtained, while on the other hand if the amount added of Ti, Zr, Be, Cr and Si is greater than 1%,
30 the alloys become brittle and hard. Moreover, insoluble elements may be produced and mirror polishing will no longer produce a fine luster of the surface of the alloys. As regards the addition of Al, Ge or Sb, the upper limit

has been found to be 5% before the workability is seriously diminished. 35

It has moreover been found that all of the above-mentioned sub-additional elements have substantially the same action and therefore can be added mixed together and will not affect
40 each other's action on the silver alloys. In fact, if more than two of these sub-additional elements are added, this is found to be more effective than if the equivalent amount of a single element is added. 45

The effect of these sub-additional elements will now be referred to in the next Example.

EXAMPLE 3

Table 3 shows the composition of twelve further alloys in accordance with the present invention, and Table 4 shows the mechanical
50 properties of the alloys. Table 4 shows the results of the examination of test performed in the same manner as already described in be connection with Example 2, with the only
55 difference that the period of immersion in hydrogen sulphide gas and artificial perspiration were respectively 10 and 60 hours.

As is apparent from Table 4, the sulphuration resistance and the mechanical strength of the alloys are greatly increased by the addition
60 of these sub-additional elements.

Taking alloy No. 15 according to the present invention as an example, it can be seen that a
65 tensile strength of about 50 to 52 kg-mm⁻² is achieved which is comparable to the hardness of brass.

Alloy No. according to the invention	Sn	In	Zn	Ag	sub-additional element
Alloy No. 12	8.3	2.1	1.0	remainder	none
" 13	8.2	2.0	0.9	"	Ti 0.2
" 14	8.3	1.9	1.0	"	Zr 0.9
" 15	8.2	1.9	1.2	"	Be 0.1
" 16	8.2	2.0	1.0	"	Cr 0.2
" 17	8.3	2.1	1.1	"	Si 0.05
" 18	8.1	2.3	1.1	"	Al 1.1
" 19	8.0	1.9	1.2	"	Ge 3.0
" 20	8.2	2.2	1.0	"	Sb 1.3
" 21	8.2	2.1	0.9	"	Ti 0.1, Al 1.3
" 22	8.3	2.0	0.9	"	Be 0.2, Cr 0.1
" 23	8.3	2.0	1.1	"	Ti 0.03, Zr 0.5, Ge 1.3

TABLE 3

Alloy No. according to the invention	Sulphuration resistance		Hv after 30% cold rolling	Colour tone
	H ₂ S gas	Artificial sweat		
Alloy No. 12	○	◎	139	silver white
" 13	◎	◎	155	"
" 14	◎	◎	163	"
" 15	◎	◎	153	"
" 16	◎	◎	165	"
" 17	◎	◎	151	"
" 18	◎	◎	163	"
" 19	◎	◎	168	"
" 20	◎	◎	159	"
" 21	◎	◎	170	"
" 22	◎	◎	162	"
" 23	◎	◎	175	"

TABLE 4

Of the sub-additional elements, Ti, Zr, Cr, Be and Si have high melting points and therefore they are first formed into mother alloys with silver at melting and then added in the form of mother alloys. Moreover, since they are easy to oxidize at high temperatures, it is desirable to use some suitable flux to melt these sub-additional elements in an inert atmosphere to prevent oxidation at melting.

In all of the alloys according to the present invention melting, founding and rolling can be relatively easily carried out, but if the amounts of tin and indium are relatively large, or if some oxides are mixed in at the melting process, malleability and ductility may be a little decreased.

In order to further improve foundability, malleability and ductility of the alloys of the present invention, it has been found that the addition of a small amount of copper has a beneficial effect. Moreover, the copper tends

to prevent segregation of other additional elements. This beneficial effect is particularly large when tin and indium are added in amounts approaching their respective upper limits, while zinc is added in an amount approaching its lower limit. It has been found that the addition of copper of more than 0.001% already has the effect discussed above. However, if the amount of copper exceeds the solution limit, the sulphuration resistance of silver can be decreased. For this reason it has been found that the best range of copper is 0.001 to 10%.

The effects in improving workability and foundability by addition of Cu will be disclosed with the explanation of the following embodiment.

EXAMPLE 4.

Table 5 shows the chemical composition of the alloys: two with Cu added the other two without Cu.

Alloy No. according to the invention	Sn	In	Zn	Ag	Cu
Alloy No. 24	6.7%	3.4%	1.8%	remainder	2%
25	7.2	1.5	1.4	"	0.4
26	6.7	3.5	1.8	"	0
27	7.4	1.6	1.5	"	0

TABLE 5

Table 6 shows the mechanical properties of the alloys shown in Table 5. Namely the yields by face scraping to remove the surface roughness, workability in rolling process etc. and the sulphuration resistance (keeping in

H₂S gas—in the same manner as shown in the Example 1) are shown. It can be understood from Table 6 that Cu has favourable effects on foundability and workability.

Alloy No. according to the invention	Ingot surface	Yield rate by face scraping	Workability	Sulphuration resistance
Alloy No. 24	good	79%	good	⊙
" 25	"	77	extremely good	⊙
" 26	average	67	average	⊙
" 27	"	64	good	⊙

TABLE 6

It will be appreciated that the addition of copper has a totally different effect from the addition of the sub-additional elements and

therefore copper can be added at the same time as the sub-additional elements without any deleterious effect.

The alloys according to the present invention have been tested not only in laboratory conditions, but also by using them to make ornaments, table-ware and watch cases and were used in the normal fashion. It has been found that the high sulphuration resistance is confirmed in practice and moreover that the alloys of the present invention have as good mechanical properties as brass, better plasticity and free cutting property than that of a free cutting brass and can therefore be widely applied to a number of industrial and practical uses.

WHAT WE CLAIM IS:—

1. A silver alloy of high sulphuration resistance having the following percentage composition by weight:

Sn	4—10%
In	0.5—12%
Zn	0.1—5%
Ag	balance.

2. A silver alloy as claimed in claim 1 containing additionally any one or more of

the metals Ti, Be, Zr, Cr and Si in an amount of 0.001—1% in total, and/or any one or more of the metals Sb, Al and Ge in an amount 0.001—5% in total.

3. A silver alloy as claimed in claim 1 or claim 2 including Cu in an amount 0.001—10%.

4. A silver alloy as claimed in claim 1 and as hereinbefore particularly described in any of the Examples.

5. A silver alloy having the following percentage composition by weight:

Sn	4—10%
In	0.5—12%
Ag	0.5—12%

6. An article made of a silver alloy as claimed in any preceding claim.

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4. A silver alloy as claimed in claim 1 and as hereinbefore particularly described in any of the Examples.

5. A silver alloy having the following percentage composition by weight:

Sn	4—10%
In	0.5—12%
Ag	0.5—12%

6. An article made of a silver alloy as claimed in any preceding claim.

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