

Semi-Bright Watchcase and Method for the Preparation thereof.

The present invention relates to a metal-made ornamental article such as a watchcase of improved semi-bright surface finish and a method for the preparation thereof.

In the prior art, it is usual that the surface of a metal-
5 made ornamental article such as a watchcase or an accessory thereof, e.g. a watchstrap, is finished by providing one or more plating layers with the object of imparting increased decorativeness and resistance to atmospheric influences. When a bright silvery surface finish with brilliant lustre is desired of a watchcase,
10 a watchcase body for example (referred to hereinafter as the substrate) made of brass or stainless steel is first provided with a plating layer of nickel and then with a plating layer of palladium. When a bright golden finish with brilliant lustre is desired, a watchcase body made of brass is first provided with a
15 plating layer of nickel and then with a plating layer of an alloy mainly composed of gold.

In contrast to the above-mentioned bright surface finishing with a noble metal, it is a trend of fashion in recent years that some people prefer watchcases and watchstraps with a dull-finished
20 or semi-bright surface capable of giving an old-fashioned or

antique impression or looking like a worn-out surface of stainless steel or gold after many years of use. It is almost impossible to obtain such a semi-bright surface finish by a conventional plating method so that according to one usual method the surface of the base body of a watchcase is subjected to a honing treatment to impart a deliberately unevenly roughened surface, before the surface is provided with an underplating layer of nickel and a finishing plating layer of palladium or of an alloy of gold.

This method of uneven honing, however, is not wholly satisfactory from the aesthetic point of view due to the appearance of the honed marks on the surface and is unable to reproduce the somewhat dull surface of stainless steel or gold which may be obtained when innumerable scratches are formed at random on a worn-out surface. It has also been proposed to apply the uneven honing treatment to a surface with an underplating layer of nickel but this method is economically unacceptable because the thickness of the underplating layer must at least be doubled, since otherwise the underplating layer is readily destroyed by the honing treatment.

The inventors have continued extensive investigations to provide a watchcase and accessories thereof having a surface finished to give an old-fashioned or antique impression of a high aesthetic value to surpass conventional bright finishing and have arrived at a discovery on the basis of which the present invention has been completed.

Thus, the semi-bright, metal-made ornamental article according to the invention comprises:

- (a) a base body of the article as a substrate made of a copper alloy or zinc, optionally having a corrosion-resistant plating layer;

(b) an underplating layer of nickel formed on the surface of the substrate; and

(c) a finishing plating layer of a noble metal selected from the group consisting of palladium, rhodium and gold or an alloy of

5 gold formed on the surface of the underplating layer, the total thickness of the underplating layer and the finishing plating layer being in the range from 2 μ m to 5 μ m and the relative reflectivity, as hereinafter defined, of the surface of the finishing plating layer being in the range from 4 to 7.

10 Such a controlled surface condition of the plating layer can be obtained by a method in which the underplating layer and the finishing plating layer are formed each by a wet-process plating procedure in a plating bath and either one or both of the plating baths in the wet-process plating procedure for the underplating
15 and finishing platings contain a brightening agent in an amount which is about a half of the amount conventionally in use.

The base body of the watchcase or the like as the substrate is necessarily made of a copper alloy, such as brass, nickel silver or the like, or zinc. Optionally the substrate surface of
20 zinc is provided with a corrosion-resistant plating layer of, for example, copper and/or nickel. The substrate surface, with or without the corrosion-resistant plating layer, is first provided with an under-plating layer of nickel and then with a finishing plating layer of a noble metal which may be palladium, rhodium,
25 gold or an alloy of gold. Optionally two or more plating layers of different noble metals are formed to provide together a finishing plating layer. These noble metals can be of a

conventional grade used in plating treatment.

The thickness of the plating layers is an important factor for achieving the object of the invention. Namely, the total thickness of the underplating layer and the finishing plating layer must be in the range from 2 μm to 5 μm . This limitation must be observed even when the finishing plating layer is formed of two or more plating layers of different noble metals. When the total thickness of the plating layers is outside this range, the appearance of the plated surface may not satisfy the requirement for the semi-bright surface condition as desired.

Various modifications are possible in the actual procedures for forming the plating layers. When semi-bright silvery finishing is desired, for example, a brass-made substrate may be first provided with a semi-bright plating layer of nickel and then with a bright plating layer or palladium. When semi-bright golden finishing is desired, on the other hand, a brass-made substrate may be first provided with a dull-surface plating layer of nickel and then with a bright plating layer of a gold alloy as the finishing plating layer. Alternatively, the finishing plating layer in this case may be composed of a bright palladium plating layer and a bright gold plating layer thereon. In short, it is not always necessary that all of the plating layers have a semi-bright surface. The semi-bright surface plating layer of nickel here implied is a plating layer obtained by a wet-process plating process in which the plating bath contains a brightening agent in an amount which is about a half of the amount conventionally used for forming a bright plating layer.

The brightening agents usable in the process according to the invention include primary brightening agents such as a compound having a $-C-SO_2-$ linkage, e.g. saccharin, sodium 1,5-naphthalene disulphonate, 1,3,6-naphthalene trisulphonate
5 and the like, and secondary brightening agents such as coumarine, 2-butyne, 2-butyne-1,4-diol, ethylene cyanhydrin, thiourea, quinoline, pyridine and the like.

When the finishing plating layer of a noble metal is desired to have a semi-bright surface, the amount of the brightening agents
10 added to this plating bath also should be about a half of that added to a plating bath for forming a bright plating layer of the same noble metal.

According to the invention the total thickness of the underplating layer and the finishing plating layer is controlled
15 in a range from 2 μm to 5 μm and the wet-process plating procedure is conducted in a plating bath containing a controlled amount of a brightening agent so as to limit the relative reflectivity of the finished surface to a value in the range from 4 to 7. The relative reflectivity here implied is a value obtained from a goniophotometric curve for the light incident at the plated surface with an
20 angle of 60° and regularly reflected by the measurement with a goniophotometer, for example the automatic goniophotometer manufactured by Murakami Shikisai Gijutsu Kenkyusho Co. Semi-bright plated surfaces of watchcases after a honing treatment
25 usually have a relative reflectivity of 9 or larger as measured with the same instrument. In this regard, the relative reflectivity of 4 to 7 according to the invention is unique.

The accompanying Figures 1a, 1b and 1c each illustrate a goniophotometric curve obtained with a goniophotometer Model GP 1-R for the surfaces obtained in the following Examples 1, 2 and 3, respectively, of the invention while Figure 1d, the peak head of which reaches the measurement ceiling, is for a conventional bright-plated surface described for comparative purposes in Example 1. These figures clearly show the matt or semi-bright condition of the surfaces according to the invention, which give an impression of high-class goods with reduced brightness. When the relative reflectivity of the plated surface is controlled within a range of 4 to 7 and the total thickness of the plating layers is controlled within a relatively narrow range, the light passing through one layer is subject to interference with the light passing through another layer to give a high aesthetic value of an old-fashioned or antique impression of the watchcase which could not be obtained by the prior art products and processes.

The invention is further described in greater detail by means of the following non-limiting Examples.

Example 1.

A brass-made base body of a watchcase was first provided with a dull-surface plating layer of nickel having a thickness of 3 μm by an electrolytic plating method in a plating bath at a temperature of 40 to 55°C with a current density of 2 to 10 A/dm^2 on the cathode. The formulation of the plating bath, which had a pH of 3.5 to 4.5, was as follows:

	Nickel sulphate	250 g/litre
	Nickel chloride	45 g/litre
	Boric acid	40 g/litre
	Sodium 1,5-naphthalene disulphonate	5 g/litre
5	1,4-Butyndiol	0.1 g/litre
	Formalin	1.2 g/litre

The thus-formed underplating layer of nickel was further provided thereon with a bright finishing plating layer of palladium having a thickness of 2 μm by an electrolytic plating method in a plating bath at a temperature of 25 to 35°C with a current density of 0.2 to 1.5 A/dm² on the cathode. The formulation of the plating bath, which has a pH of 8.5 to 9.5, was as follows:

	Palladium chloride	5 g/litre
	Nickel chloride	30 g/litre
15	Ammonium chloride	50 g/litre
	Brightening agent	3-5 g/litre

The brightening agent was a commercial product sold under the trade name of Eugilite No. 61 manufactured by Ebara Eugilite Co. of which the principal ingredient was O-hydroxy coumaric anhydride.

For comparison, the same plating procedures as above were undertaken except that the underplating of nickel was performed using a conventional plating bath for a bright nickel plating. The relative reflectivity of the surface of the thus-finished watchcase was at least 9 and no semi-bright surface could be obtained.

Example 2.

A brass-made base body of a watchcase was first provided

with a bright plating layer of nickel having a thickness of 1 μm by an electrolytic plating method in a plating bath at a temperature of 50 to 70°C with a current density of 0.5 to 6 A/dm^2 on the cathode. The formulation of the plating bath, which had a pH of 4 to 4.5, was as follows:

	Nickel sulphate	280 g/litre
	Nickel chloride	40 g/litre
	Boric acid	40 g/litre
	Brightening agent	3 g/litre
10	Pit inhibitor	5 g/litre

The brightening agent used above was the same as in the plating bath for palladium plating in Example 1.

Thereafter, the nickel-plated substrate was provided with a dull-surface plating layer of palladium having a thickness of 2 μm by an electrolytic plating method in a plating bath at a temperature of 25 to 35°C with a current density of 0.2 to 1.5 A/dm^2 on the cathode. The formulation of the plating bath, which had a pH of 8.5 to 9.5, was as follows. The brightening agent was the same one as used in the nickel plating.

20	Palladium chloride	8 g/litre
	Nickel chloride	40 g/litre
	Ammonium chloride	8.8 g/litre
	Brightening agent	1.2 g/litre

Further, the thus palladium-plated surface was provided with a bright plating layer of a gold alloy having a thickness of 1 μm by an electrolytic plating method in a plating bath at a temperature of 45 to 50°C with a current density of 0.2 to

1.0 A/dm² on the cathode. The formulation of the plating bath, which had a pH of 9 to 9.5, was as follows:

	Sodium gold sulphite	0.5 g/litre
	Palladium (as metal)	3.0 g/litre
5	EDTA-Zn	1.0 g/litre
	Arsenious acid	1.0 g/litre
	EDTA-2Na	100 g/litre

Example 3.

A zinc-made watchcase was first provided with a corrosion-resistant plating composed of a layer of copper of a bright surface having a thickness of 15 to 20 μ m and a layer of nickel of bright surface having a thickness of 10 to 15 μ m. The copper plating was performed in a plating bath of the formulation shown below at a temperature of 50°C with a current density of 0.5 to 5 A/dm² on the cathode while the nickel plating was performed using the same plating bath and under the same conditions as in the bright nickel plating in Example 2.

	Copper sulphate	200 g/litre
	Sulphuric acid	50 g/litre
20	Phenol	1 g/litre
	Thiourea	0.01 g/litre
	Dextran	0.01 g/litre

In the next place, a dull-surface plating layer of nickel having a thickness of 2 μ m was provided on the above-described corrosion-resistant plating layer using the same plating bath and under the same conditions as in Example 1. Finally, a bright-surface palladium plating layer having a thickness of 2 μ m

was formed on the underplating layer of nickel using the same plating bath and under the same conditions as in Example 1. The thus-finished palladium-plated silvery surface had a relative reflectivity of 6.4.

5. When the above-mentioned bright-surface palladium plating was omitted and, instead, a bright-surface gold-alloy finishing plating was performed using the same plating bath and under the same conditions as in Example 2, a watchcase having a semi-bright golden surface could be obtained.



CLAIMS

1. A semi-bright, metal-made ornamental article which comprises:
 - (a) a base body of the article as a substrate made of a copper alloy or zinc;
 - (b) an underplating layer of nickel formed on the surface of the substrate; and
 - (c) a finishing plating layer of a noble metal selected from the group consisting of palladium, rhodium and gold or an alloy of gold formed on the surface of the underplating layer, the total thickness of the underplating layer and the finishing plating layer being in the range from 2 μm to 5 μm and the relative reflectivity, as hereinbefore defined, of the surface of the finishing plating layer being in the range from 4 to 7.
2. A method for the preparation of a semi-bright, metal-made ornamental article, which method comprises the steps of:
 - (a) providing a base body of the article made of a copper alloy or zinc on the surface thereof with an underplating layer of nickel formed in a first electrolytic bath containing a brightener; and
 - (b) forming a finishing plating layer of a noble metal selected from the group consisting of palladium, rhodium and gold or an alloy of gold on the surface of the underplating layer in a second electrolytic plating bath containing a brightener,



the total thickness of the underplating layer and the finishing plating layer being in the range from 2 μm to 5 μm and the concentration of the brightener in either one or both of the electrolytic baths being selected such that the relative
5 reflectivity, as hereinbefore defined, of the surface is in the range from 4 to 7.

3. A method for the preparation of a semi-bright, metal-made ornamental article, said method being as claimed in claim 2 and substantially as hereinbefore described in any of the foregoing
10 Examples.

4. A semi-bright, metal-made ornamental article when made by a method as claimed in claim 2 or claim 3.
