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Watch-cases and accessories — Gold alloy coverings —

Part 2:
Determination of fineness, thickness, corrosion resistance and adhesion

Boîtes de montres et leurs accessoires — Revêtements d'alliage d'or —

Partie 2: Détermination du titre, de l'épaisseur, de la résistance à la corrosion et de l'adhérence

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 114, *Horology*, Subcommittee SC 6, *Precious metal coverings*.

This fourth edition cancels and replaces the third edition (ISO 3160-2:2003), of which it constitutes a technical revision.

ISO 3160 consists of the following parts, under the general title *Watch-cases and accessories — Gold alloy coverings*:

- *Part 1: General requirements*
- *Part 2: Determination of fineness, thickness, corrosion resistance and adhesion*

Introduction

Gold alloy coatings deposited on watch-cases and their accessories have to comply with technical, decorative requirements and have to also satisfy national rules about precious metals.

This part of ISO 3160 aims to specify coating characterization methods to qualify their corrosion resistance and their adhesion to the substrate concerning esthetical and technical aspects, and to specify methods to determine thickness and gold fineness of these coatings to check that they satisfy the requirements of ISO 3160-1.

Watch-cases and accessories — Gold alloy coverings —

Part 2:
Determination of fineness, thickness, corrosion resistance and adhesion

1 Scope

This part of ISO 3160 specifies methods to determine fineness, thickness, corrosion resistance and adhesion for gold alloy coverings on watch-cases and accessories, including bracelets when they are permanently attached to the case.

The tests apply only to significant surfaces.

This part of ISO 3160 applies to all gold alloy coverings specified in ISO 3160-1.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1463, *Metallic and oxide coatings — Measurement of coating thickness — Microscopical method*

ISO 2177, *Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution*

ISO 3160-1, *Watch-cases and accessories — Gold alloy coverings — Part 1: General requirements*

ISO 3497, *Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods*

ISO 3543, *Metallic and non-metallic coatings — Measurement of thickness — Beta backscatter method*

ISO 3868, *Metallic and other non-organic coatings — Measurement of coating thicknesses — Fizeau multiple-beam interferometry method*

ISO 4538, *Metallic coatings — Thioacetamide corrosion test (TAA test)*

ISO 9220, *Metallic coatings — Measurement of coating thickness — Scanning electron microscope method*

ISO 9227, *Corrosion tests in artificial atmospheres — Salt spray tests*

ISO 11426, *Jewellery — Determination of gold in gold jewellery alloys — Cupellation method (fire assay)*

ISO 12687, *Metallic coatings — Porosity tests — Humid sulfur (flowers of sulfur) test*

ISO 14647, *Metallic coatings — Determination of porosity in gold coatings on metal substrates — Nitric acid vapour test*

ISO 27874, *Metallic and other inorganic coatings — Electrodeposited gold and gold alloy coatings for electrical, electronic and engineering purposes — Specification and test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
significant surface
part of the surface which is to receive the gold alloy covering and which is essential to the appearance and serviceability of the component

Note 1 to entry: When there is no agreement between the supplier and customer, a significant surface is considered to be any surface which can be touched by a 5 mm diameter ball.

4 General

In the context of this part of ISO 3160, the term “corrosion” includes tarnishing and oxidation, as well as surface penetration and the effects of the penetration of corrosive agents into porosity and micro-discontinuities of the protection.

It is generally required that, except where specified to the contrary, gold-alloy-covered surfaces should not have suffered any damage after each of the proposed tests. In practice, however, this condition is never strictly fulfilled and certain minor changes are observed, especially at the edges of the gold-covered parts. Consequently, interpretation of the results requires a certain amount of common sense and, if necessary, agreement between the supplier and customer. The presence of such almost inevitable faults makes it impossible to sell the tested item as new. In this respect, the tests are therefore to be considered to be destructive.

The test methods apply to all gold alloy coverings specified in ISO 3160-1.

5 Determination of gold fineness

5.1 General

If the fineness is measured on a gold alloy covering which is separated from the base metal, the method used to separate the gold alloy covering from the base metal shall not affect the fineness of the gold covering to a significant extent.

For multilayer coverings, the covering content measured is the mean content, which shall be a minimum of 585 parts per thousand, in accordance with ISO 3160-1.

The method of separation of the sample is specified in Annex A.

5.2 Methods of gold fineness determination

Any of the following methods shall be used for the determination of contents:

a) chemical analysis by reduction in an aqueous solution of, for example, sulfur dioxide or any other suitable reducing agent;

b) analysis by

    1) cupellation (fire test) as specified in ISO 11426,

    2) Energy Dispersive Spectroscopy on Scanning Electron Microscopy (SEM/EDS),

    3) atomic absorption spectrometry,

    4) spectrophotometry,

    5) X-ray spectrometry as specified in ISO 3497,

    6) plasma emission spectrometry (ICP method);

c) touchstone method (only to be used to evaluate the approximate fineness);

d) any other physico-chemical method.

Any method used shall be capable of giving an indication of fineness to within an accuracy of 50 parts per thousand.

In the event of arbitration, cupellation and SEM/EDS are the reference methods.

The implementation of the two reference methods is described in Annex B.

6 Determination of thickness

Any of the following test methods for the determination of the thickness of gold alloy coatings shall be used, provided a measuring accuracy of ±10 % is guaranteed:

a) the microsection method specified in ISO 1463 for a thickness of 5 µm (−20 %) and above (local thickness);

b) the dissolution method and chemical analysis for any thickness of gold alloy covering (average thickness) specified in ISO 27874;

c) dissolution and measurement by the micrometer method specified in ISO 1463;

d) the beta-ray backscatter method specified in ISO 3543;

e) the X-ray spectrometric method (fluorescence) specified in ISO 3497;

f) the coulometric method (coulometric method by anodic dissolution) specified in ISO 2177;

g) the fizeau multiple-beam interferometry method specified in ISO 3868;

h) the scanning electron microscope method specified in ISO 9220;

i) any other physical-chemical method which can guarantee accuracy.

In the event of arbitration, the microsection method specified in ISO 1463 shall be used (local thickness).

7 Determination of the corrosion resistance

7.1 Forms of corrosion

The various forms of corrosion which appear on a gold-alloy-covered article may be divided into three groups.

a) Corrosion of the base metal at points where there are gaps in the covering: electrochemical cells may act at these points and accelerate penetration, and also at the boundary between the covering and the base metal.

b) Attack caused by saline agents or possibly by mildly acidic agents (contact with perspiration, packaging, leathers or certain plastics): the products of corrosion may be of various colours, i.e. orange, violet, blue, green or brown.

c) Attack caused by sulfur-containing agents (atmospheric hydrogen sulfide, vulcanized rubber, etc.): such agents may also attack the base metal at points where there are gaps in the protective covering. In addition, they cause changes in the surface colouring, which may even turn matt and black.

The proposed tests make it possible for these various effects to be distinguished to a certain extent. Gold alloy coverings shall be resistant in all the environments described below. According to the nature of the article, the supplier may, with the agreement of the customer, determine the number of items to be submitted to each test.

The development of corrosion is closely allied to the relative humidity of the ambient environment.

7.2 Sampling and preparation

7.2.1 General

According to the nature of the article, the supplier may, with the agreement of the customer, determine the number of items to be submitted to each test and the test conditions. The test conditions shall be stated in the test report.

The tests for determination of the corrosion resistance are applicable to finished items in the condition in which they are supplied to customers. They can also be applied during manufacture, but any interpretation of results shall take into account the form which the item will take when in its final condition.

7.2.2 Test of finished items (ready-for-use condition)

If the item to be tested is delivered in the ready-for-use condition, no cleaning operation shall be carried out. It is well known that residues remaining after insufficient rinsing have a considerable effect on tarnishing. It is necessary for the item to be tested in the condition in which it will be received by the customer.

7.2.3 Test of coating process (without passivation treatment)

When testing the quality of the coating on significant surfaces, care shall be taken to avoid any unusual influence. The sample shall be completely cleaned, first by the use of a water-based detergent with ultrasonic agitation, then in a solution of distilled water and ethanol or isopropanol. Degreasing in a chlorinated solvent is insufficient.

7.2.4 Non-significant surfaces

The non-significant surfaces of the object shall be coated with a lacquer or a covering which is sufficiently resistant to prevent any attack on the protected metal throughout the duration of the test.

7.3 Continuity of the covering (porosity test)

7.3.1 General

In practice, for the porosity test, it is recommended that account can be taken of the tests given in ISO 10308[4].

7.3.2 Test for a copper-containing base metal with or without nickel, and die-cast zinc-based alloys

7.3.2.1 Test vessel

Use a suitable closed vessel, made of glass or acid-resistant plastic, and expose the sample to the corrosive atmosphere on all sides.

7.3.2.2 Test solution

The solution shall be of the following composition:

- acetic acid: (CH_3COOH, ρ_{20} = 1,048 g/cm^3 to 1,052 g/cm^3, ≥ a mass fraction of 99,0 %): a mass fraction of 50 %;
- deionized water: a mass fraction of 50 %.

The vessel shall be filled with this solution to a height of about 10 mm. The walls of the vessel shall be lined with thick white blotting paper which dips into the liquid.

7.3.2.3 Position of the sample

The sample shall be suspended on a glass hook at a distance of at least 30 mm from the liquid and the walls of the vessel.

7.3.2.4 Temperature during the test

The temperature during the test shall be (23 ± 2) °C.

7.3.2.5 Duration of the test

The duration of the test shall be 24 h.

7.3.2.6 Criteria

When observed, the sample shall not reveal to the naked eye either green droplets or accumulations of green deposits anywhere on the significant surface. On die-cast zinc-based alloys, no white deposit shall appear.

7.3.3 Test a ferrous base metal

7.3.3.1 Test vessel

The test shall be carried out in a suitable closed vessel made of glass or acid-resistant plastic, in which the sample is exposed to a corrosive atmosphere on all sides.

7.3.3.2 Test solution

The solution shall have the following composition:

- crystalline sodium metabisulfite ($Na_2S_2O_5$ p.a. ACS, synonyms: sodium pyrosulfite, sodium disulfite): a mass fraction of 45 %;
- deionized water: a mass fraction of 55 %.

The vessel shall be filled with this solution to a height of about 10 mm. The walls of the vessel shall be lined with thick white blotting paper which dips into the liquid.

7.3.3.3 Position of the sample

The sample shall be suspended on a glass hook at a distance of at least 30 mm from the liquid and the walls of the vessel.

7.3.3.4 Temperature during the test

The temperature during the test shall be (23 ± 2) °C.

7.3.3.5 Duration of the test

The duration of the test shall be 24 h.

7.3.3.6 Criteria

When observed, the sample shall not reveal to the naked eye any traces of corrosion anywhere on the significant surface. Slight general tarnishing of low-carat coatings is admissible.

7.3.4 Non-determination of base metal

Where the base metal cannot be determined, use the test described in 7.3.2.

7.3.5 Testing with nitric acid vapour

The test shall be carried out as specified in ISO 14647.

7.4 Synthetic perspiration test

7.4.1 Test vessel

The test shall be carried out in a closed Pyrex®[1] glass (or equivalent) vessel, which can be heated to 40 °C.

7.4.2 Test solution

The solution used shall have the following composition:

- sodium chloride ($NaCl$ p.a. ACS, ISO): 20 g/l;
- ammonium chloride (NH_4Cl p.a. ACS, ISO): 17,5 g/l;
- urea (NH_2CONH_2 p.a. ACS, ≥ a mass fraction of 99,5 %, synonyms: carbamide, carbonyl diamine): 5 g/l;
- acetic acid (CH_3COOH, ρ_{20} = 1,048 g/cm^3 to 1,052 g/cm^3, ≥ a mass fraction of 99,0 %): 2,5 g/l;
- racemic lactic acid [$CH_3CH(OH)COOH$, ρ_{20} = 1,21 g/cm^3, very pure ph Eur, BP, E 270, about a mass fraction of 90 %, synonyms: (±) −2-hydroxypropanoic acid, lactol]: 15 g/l;
- sodium hydroxide ($NaOH$ p.a. ISO, synonym: caustic soda) in solution (concentration: 80 g/l): quantity required of the solution to bring the pH to 4,7.

The vessel shall be filled with the solution to a height of about 10 mm.

A fine mist of the same solution shall then be sprayed over the surface of the sample using a glass sprayer, and the sample shall immediately be placed in the test atmosphere.

7.4.3 Position of the sample

The sample shall be suspended on a glass hook at a distance of at least 30 mm from the liquid and the walls of the vessel.

NOTE Samples which cannot be suspended may be laid on some cotton soaked with synthetic perspiration, but the reproducibility is not so good.

7.4.4 Temperature during the test

The temperature during the test shall be (40 ± 2) °C.

7.4.5 Duration of the test

The duration of the test shall be at least 24 h.

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[1] Pyrex® is an example of suitable glassware available commercially. This information is given for the convenience of the users of this part of ISO 3160 and does not constitute an endorsement by ISO of this product.

7.5 Neutral saline mist test

7.5.1 General

The neutral saline mist test shall be carried out as specified in ISO 9227.

7.5.2 Criteria

After washing with water, the general colouring of the coating shall not have changed when compared with an untested control sample. The appearance of a light layer of tarnish may be tolerated, provided that it can be removed by wiping the sample. Slight general tarnishing of low-carat coatings is admissible. No saline deposits shall appear, nor corrosion stains.

7.6 Test of the effects of agents containing sulfur

7.6.1 Thioacetamide test

The test specified in ISO 4538 shall be carried out for a period of 48 h.

7.6.2 Flowers of sulfur test in a moist atmosphere

The test shall be carried out as specified in ISO 12687.

8 Adhesion test

The adhesion tests of the different gold alloy coatings shall meet the requirements of ISO 27874. They shall be the subject of a preliminary agreement between the supplier and customer.

Annex A
(normative)

Method of obtaining a sample of gold alloy covering

A.1 General

In order to bring the gold alloy covering to a form suitable for analysis and in order to determine its mass, it is necessary to separate it from the base metal.

The gold content is then determined by one of the methods described in Clause 5. Since complete mechanical separation is possible only in the minority of cases, this process is carried out by dissolution of the base metal. In order to avoid any attack on the gold alloy covering, the time of exposure to the acid should be kept to a minimum. This may be ensured by one of the following measures.

a) The corners and edges of the test sample or part of it shall be chamfered by filing, etc., in order to increase the area of attack. Some of the gold alloy covering will inevitably be lost in this process. However, no error will occur since this method is concerned only with the fineness of the gold alloy covering, not with the total amount of gold on the sample.

b) The base metal is first removed as far as possible by mechanical means (by filing, milling, turning, etc.) and the residual base metal dissolved in acid.

c) A sufficient quantity of the gold alloy covering is removed as far as possible by mechanical means (for example by scraping) and any adhering base metal removed by dissolution in acid.

A.2 Dissolution of the base metal

For copper, nickel and iron alloys which are not passivated, nitric acid, 1,1 g/ml (1 volume of concentrated nitric acid to 4 volumes of distilled water), is used. For gold alloy coverings of inferior fineness to 700 parts per thousand, a more dilute nitric acid, for example 1,05 g/ml (1 volume of concentrated nitric acid to 9 volumes of distilled water), should be used. The time for complete dissolution will be longer in the more dilute acid. If the solution of the base metal becomes cloudy (due to the presence of tin), 2 % of hydrofluoric acid or 5 % of tetrafluoroboric acid can be added to the solution to avoid this problem (in a polypropylene vessel).

For stainless steel, hydrochloric acid, 1,125 g/ml (5 volumes of concentrated hydrochloric acid to 3 volumes of distilled water), is used. Aluminium alloys may be dissolved in a mass fraction of 10 % sodium hydroxide solution. Generally, such samples have undercoats of copper and/or nickel which are not attacked by sodium hydroxide. These undercoats shall therefore be dissolved in dilute nitric acid as described above, after complete dissolution of the aluminium base metal.

In each case, the base metal and undercoats (if any) are dissolved by heating the dissolving medium to a temperature of 90 °C to 95 °C. After complete dissolution of the base metal, the solution is decanted, the residual coating washed several times, first with dilute nitric acid and then with distilled water, and dried at 100 °C.

Certain gold alloy coverings will disintegrate completely after dissolution of the base metal. In this case, the solution is filtered through a weighed filtering crucible, then the residual gold alloy coating is washed and dried as described above.

Special care should be taken with tin-containing base metals, as the stannic hydroxide formed clings obstinately to the gold alloy covering. In order to avoid any excessive precipitation of stannic hydroxide, hydrofluoric acid or tetrafluoroboric acid shall be added as indicated in the first paragraph of this clause. To avoid the use of hydrofluoric or tetrafluoroboric acid, it is recommended that the nitric acid be changed several times, so as to avoid the annoying precipitation of stannic hydroxide. One should also avoid boiling the solution. Following complete dissolution of the base metal, the remaining gold alloy covering is washed in distilled water and then treated in hot hydrochloric acid (1 part concentrated hydrochloric acid to 9 parts distilled water) in order to ensure the complete dissolution of the adhering stannic hydroxide. The remaining gold alloy covering is washed and dried as described above.

A.3 Analysis of the gold alloy covering

The remaining gold alloy covering obtained by dissolution of the base metal and undercoats (if any) is weighed and subjected to analysis by one of the methods described in 5.2. Reference should also be made to ISO 27874 and to standard books on analysis of noble metals, for example, see Reference [5].

In spite of the precautions taken, it will not always be possible to avoid chemical attack on the gold alloy covering during dissolution of the base metal. If this should occur, erroneously high results will be obtained. To avoid this error, the following method, which involves the dissolution of the gold alloy covering instead of the base metal, may be used.

The test sample is weighed accurately and covered with a stop-off lacquer on all sides except for the area on which the fineness of the gold alloy covering is to be determined. An area of 0,1 cm^2 is the minimum that should be taken. The gold alloy covering is then dissolved anodically in a suitable electrolyte, which either does not attack the underlying metal or, if so, only at a higher voltage. Commercial electrolytes are available from manufacturers of coulometric plating thickness meters. The dissolution of the gold alloy covering is followed by measuring the cell voltage. The end-point is indicated by a sharp rise of cell voltage when the base metal or undercoat is exposed. The electrolysis is then immediately stopped. The resulting solution is subjected to chemical analysis for gold, preferably by atomic absorption spectrometry. The fineness of the gold alloy covering is calculated from the gold content of the solution and the loss in mass of the sample. A precision in weighing of at least 2 % is essential to attain sufficient accuracy of results.

Details of this method are specified in ISO 2177.

Annex B
(normative)

Implementation of the reference methods for the determination of gold alloy coating fineness

B.1 Cupellation

Cupellation is carried out after substrate dissolution (see Annex A). The mass of the remaining gold alloy covering shall be sufficient, preferably higher or equal to 125 mg.

The risk to modify the fineness of the gold alloy coating by the substrate chemical dissolution is more important when the content in gold is low and when the substrate is a copper alloy.

NOTE Generally, good conditions for cupellation are obtained with a minimal coating thickness of 3 µm and with a minimal gold alloy coating fineness of 585 parts per thousand.

B.2 SEM/EDS

Analyses by SEM/EDS are carried out on metallographic cross-section taken from a zone decided by agreement between the contracting parties. At least 4 measures are done.

For the preparation of the metallographic cross-section, the sample is previously covered by a galvanic coating of one or several element(s) which is (are) different(s) from elements that constitute the gold alloy coating. Then, the whole (sample and coating) is embedded in an electrical conductive resin (carbon loaded resin, for example).

The advisable value of coating's thickness is at least 1,5 µm, because of the interaction volume of the beam with the material which must be lower than the coating's thickness.

The following parameters are recommended:

- vacuum: from 10^{-3} Pa to 10^{-5} Pa;
- accelerating voltage: from 15 kV to 20 kV; in this case it is advised to analyse gold using M peaks X-rays because quantitative analysis is more efficient with M peaks than with L peaks for gold;
- timeout acquisition between 20 % and 30 %.

The test report contains parameters used, particularly the nature of electron supply, the timeout acquisition and the correction mode used to suppress matrix effects.

In the event of multi-layers coatings and if each layer has a thickness higher than 1,5 µm, it is possible to calculate an approached value of the global mean fineness of the multi-layers coating with the values of individual fineness of each layer, determined by SEM/EDS analyses, with the Formula (B.1):

$$F_m = \frac{F_1 t_1 + F_2 t_2 + \ldots F_n t_n}{t_1 + t_2 + \ldots t_n} \qquad \text{(B.1)}$$

where

F_m global mean fineness;

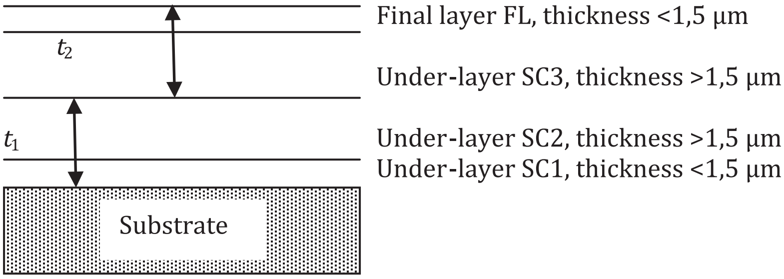
$F_1, F_2, \ldots F_n$ respective mean fineness of layers 1, 2, ...*n*;

t_1, t_2, ...t_n	respective thickness of layers 1, 2, ...n.

In the event of multi-layers coatings, and where the thickness of some layers is lower than 1,5 µm (the case of colouring coating or strike coating, for example), the fineness measure is done for layers with a thickness higher than 1,5 µm and the global mean fineness takes in account thicknesses of all layers.

Thicknesses of the considered layers are preferably measured at the same place on the sample than the place where the fineness is determined by EDS according to C.7.

For example:



The global mean fineness F_m could be calculated by the Formula (B.2):

$$F_m = \frac{F_{SC2}t_1 + F_{SC3}t_2}{t_1 + t_2} \tag{B.2}$$

where

F_{SC2}	fineness of under-layer SC2;
F_{SC3}	fineness of under-layer SC3;
t_1	thickness of SC1 + SC2;
t_2	thickness of SC3 + FL.