INTERNATIONAL STANDARD

ISO 3160-2

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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

Reference number
ISO 3160-2:1992(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 3160-2 was prepared by Technical Committee ISO/TC 114, *Horology*, Sub-Committee SC 6, *Precious metal coverings*.

This second edition cancels and replaces the first edition (ISO 3160-2:1982), of which has been technically revised.

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*

— *Part 3: Abrasion resistance tests of a type of coating on standard gauges*

Annexes A and B form an integral part of this part of ISO 3160. Annex C is for information only.

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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 standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 3160. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 3160 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 1463:1982, *Metallic and oxide coatings — Measurement of coating thickness — Microscopical method.*

ISO 2177:1985, *Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution.*

ISO 3160-1:1982, *Watch cases and accessories — Gold alloy coverings — Part 1: General requirements.*

ISO 3497:1990, *Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods.*

ISO 3543:1981, *Metallic and non-metallic coatings — Measurement of thickness — Beta backscatter method.*

ISO 3868:1976, *Metallic and other non-organic coatings — Measurement of coating thicknesses — Fizeau multiple-beam interferometry method.*

ISO 4524-1:1985, *Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 1: Determination of coating thickness.*

ISO 4524-4:1985, *Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 4: Determination of gold content.*

ISO 4524-5:1985, *Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 5: Adhesion tests.*

ISO 4538:1978, *Metallic coatings — Thioacetamide corrosion test (TAA test).*

ISO 9220:1988, *Metallic coatings — Measurement of coating thickness — Scanning electron microscope method.*

3 Definition

For the purposes of this part of ISO 3160, the following definition applies.

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

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 gaps in the surface 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 fineness

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.

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

5.1 Basic method

The method of analysis by cupellation is recommended.

5.2 Secondary methods

The following methods may also be used:

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

b) analysis by

— atomic absorption spectrometry,

— spectrophotometry,

— X-ray fluorescence spectrometry,

— atomic 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.

6 Determination of thickness

The test methods for the determination of the thickness of gold alloy coatings are defined in annex B.

6.1 Basic methods

The following methods are recommended:

a) dissolution and chemical analysis for any thickness of gold alloy covering (average thickness);

b) microsection method for a thickness of 5 µm (− 20 %) and above (local thickness).

The microsection method specified in ISO 1463 shall be used for arbitration (local thickness).

6.2 Secondary methods

Where there is no dispute, the following methods may be used:

a) dissolution and measurement by the micrometer method;

b) beta-ray backscatter method (see ISO 3543);

c) X-ray spectrometric method (fluorescence) (see ISO 3497);

d) coulometric method (see ISO 2177);

e) interferometric method (see ISO 3868);

f) scanning electron microscope method (see ISO 9220).

7 Determination of the corrosion resistance

7.1 General

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: 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

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.

7.2.1 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 great effect on tarnishing. It is necessary that the item is tested in the condition in which it will be received by the customer.

7.2.2 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, then in a mixture of distilled water and ethanol or isopropanol. Degreasing in a chlorinated solvent is insufficient.

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

7.3.1.1 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.

7.3.1.2 Test solution

The solution shall be of the following composition:

— pure concentrated acetic acid: 50 % (*m/m*)

— water: 50 % (*m/m*).

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

7.3.1.3 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.

7.3.1.4 Temperature during the test

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

7.3.1.5 Duration of the test

The duration of the test shall be 24 h.

7.3.1.6 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 alloys, no white deposit shall appear.

7.3.2 Test for an iron-containing base metal

7.3.2.1 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.

7.3.2.2 Test mixture

The supersaturated mixture shall have the following composition:

— crystalline sodium metabisulfite ($Na_2S_2O_5$): 45 % (*m/m*)

— water: 55 % (*m/m*).

The vessel shall be filled with this solution to a depth of about 10 mm. Its walls 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 °C ± 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 nacked eye any traces of corrosion anywhere on the significant surface. Slight general tarnishing of low-carat coatings is admissible.

7.3.3 Non-determination of base metal

Where the base metal cannot be determined, use the test described in 7.3.1.

7.4 Testing with saline and acidic agents (synthetic perspiration test)

7.4.1 Test vessel

The test shall be carried out in a closed Pyrex 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: 20 g/l

— ammonium chloride: 17,5 g/l

— urea: 5 g/l

— acetic acid: 2,5 g/l

— lactic acid: 15 g/l

— sodium hydroxide: quantity required to bring the pH to 4,7.

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

Then, a fine mist of the same solution shall 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 1 Samples which cannot be suspended may be laid on some cotton soaked with synthetic perspiration, but the reproducibility is less good.

7.4.4 Temperature during the test

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

7.4.5 Duration of the test

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

7.4.6 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.

7.5 Test of the effects of agents containing sulfur

Carry out the thioacetamide test specified in ISO 4538 for a period of 48 h.

8 Adhesion test

The adhesion tests of the different gold alloy coatings shall meet the requirements of ISO 4524-5. 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 Introduction

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 5.1 and 5.2. 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, $\varrho = 1,1$ 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 thousandths, a more dilute nitric acid, for example $\varrho = 1,05$ 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 a problem appears (due to the presence of tin) concerning the solution of the base metal, 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, $\varrho = 1,125$ g/ml (5 volumes of concentrated hydrochloric acid to 3 volumes of distilled water), is used. Aluminium alloys may be dissolved in 10 % (*m/m*) 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, then with distilled water and dried at 110 °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.

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 5.1 and 5.2. Reference should also be made to ISO 4524-4 and to standard books on analysis of noble metals, for example, reference [3].

NOTE 2 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.

For details of this method, reference should be made to ISO 2177.