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Metallic coatings — Porosity tests — Humid sulfur (flowers of sulfur) test

*Revêtements métalliques — Essais de porosité — Essai à la fleur de
soufre par voie humide*



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Foreword

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Metallic coatings — Porosity tests — Humid sulfur (flowers of sulfur) test

1 Scope

This International Standard specifies a method of revealing discontinuities and porosity in metallic coatings, where they penetrate the coating layer or layers down to a silver, copper or copper-alloy substrate.

This method is especially useful for coatings consisting of single or combined layers of any coating that does not significantly tarnish in a reduced-sulfur atmosphere, such as gold, nickel, tin, tin-lead palladium and their alloys.

This test method is designed to show whether or not the coating meets the requirement concerning an acceptable porosity level specified by the user. The value specified is usually determined by user's experience to be acceptable for the intended application.

Recent reviews of porosity testing and test methods can be found in the literature [1], [2]. An ISO general guide to porosity tests for metallic and other inorganic coatings is available as ISO 10308:1995, *Metallic coatings — Review of porosity tests*.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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 2079:1981, *Surface treatment and metallic coatings — General classification of terms*.

ISO 2080:1981, *Electroplating and related processes — Vocabulary*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

3 Definitions

For the purposes of this International Standard, the following definitions apply (other relevant definitions can be found in ISO 2079 and ISO 2080).

3.1 corrosion products: Chemical products, derived from the substrate that usually protrude from the surface at discontinuities. The chemical reaction products form during the test and can be readily examined after the test exposure. They cannot be readily removed by mild air dusting [see clause 10, item b) 2].

3.2 discontinuity: Any opening through an otherwise continuous coating. Typically the openings are pores or cracks in the coating. They may also be voids or breaks in the coating caused by mechanical damage such as scratches or non-conductive inclusions in the basis materials.

3.3 measurement area: In this method, that portion or portions of the surface that is examined for the presence of porosity. The measurement area may be indicated on the drawings of the parts or by the provision of suitably marked samples.

3.4 metallic coatings: Autocatalytic coatings, chemical (non-electrolytic) platings, claddings, electroplatings and hot-dip coatings applied to the substrate. The coating may comprise a single metallic layer or a combination of metallic layers.

3.5 pore: A hole, typically microscopic in size and randomly located, often with a circular shape, that penetrates through the coating to an underlying coating or the basis-metal.

3.6 porosity: The presence of any crack, discontinuity, hole or scratch in the coating that exposes a different underlying metal.

3.7 significant surface: That portion or portions of the coating surface that is essential to the serviceability or function of the part, or which can be the source of corrosion products or tarnish films that interfere with the function of the part. For many coated products, the significant surface is identical to the measurement area.

3.8 tarnish: The reaction products of copper or silver with oxygen or reduced sulfur (i.e. H_2S and elemental sulfur vapour, but not SO_2 or other sulfur oxides). They consist of thin films or marks and spots that do not protrude significantly from the surface of the metallic finish (in contrast with corrosion products).

3.9 tarnish creepage: Movement of tarnish films across the surface of the coating. The tarnish originates either from pores or cracks in the coating or from areas of bare basis metal near the measurement area (as in a cut edge). It is also called creep corrosion.

3.10 underplate: A metallic coating layer between the substrate and the topmost layer or layers. The thickness of an underplate is usually greater than 1 μm . There may be more than one.

4 Principle

This test relies on the formation of basis metal or underplate sulfides and oxides, formed by reaction with sulfur vapour in a humid atmosphere and exposed through discontinuities in the metallic coating. The sulfide corrosion products of both silver and copper and copper oxide form black or brown-coloured markings or spots that are readily observed by visual inspection.

5 Summary of method

Test specimens are suspended over flowers of sulfur (powdered sulfur) in a container equipped with a vent and at controlled, elevated relative humidity and temperature. Elemental-sulfur vapour, which always exists in equilibrium with sulfur powder in a closed system, attacks any exposed copper, copper alloy, silver or silver alloy such as that found at the bottom of pores. Brown or black tarnish marks or spots indicate porosity.

Exposure periods may vary, depending on the extent of porosity to be revealed.

This test involves tarnish or oxidation (corrosion) reactions in which the corrosion products delineate defect sites in coatings. The chemistry and properties of the corrosion products formed as a result of the test usually do not

resemble those found in natural or service environments. Therefore, this test is not recommended for prediction of product performance unless correlation is first established with service experience.

6 Reagents

6.1 Purity

The potassium nitrate used shall be of recognized analytical-reagent grade. The water used shall be distilled or deionized and have a conductivity not greater than $20 \mu\text{S}/\text{cm}$ (measured as specified in ISO 3696). The sulfur shall be of commercial laboratory grade.

6.2 Potassium nitrate solution

Prepare a saturated solution of potassium nitrate (KNO_3) by adding approximately 200 g of the reagent to approximately 200 ml of water (see 6.1).

NOTE — The saturated solution will contain undissolved potassium nitrate salt. This condition is necessary to achieve a constant-humidity atmosphere above the solution.

6.3 Dry reagent

Sulfur, precipitated (flowers of sulfur).

7 Apparatus

7.1 Test vessel, consisting of any convenient-sized transparent vessel of glass or acrylic resin (or any other material that it not affected by high humidity or sulfur), such as a glass desiccator of approximately 10 litre capacity. It shall have a lid or cover with an access hole capable of being plugged with a stopper. The hole shall be large enough to allow the insertion of the humidity sensor with a remote read-out device into the vessel. The stopper shall contain a 1 mm to 4 mm diameter hole to serve as a vent.

7.2 Sample supports, designed as holders or hangers and made from material such as glass, acrylic resin or polypropylene which will not be affected by sulfur or high humidity, and arranged so that the test specimen will be at least 75 mm distance from the humidity-controlling solution and the sulfur powder (see 7.3). The test specimen shall also be at least 25 mm from the vessel walls and at least 10 mm from other test specimen and other surfaces. Do not use a desiccator plate as a primary support; it may be used as an under-support. The fixture and any supports shall not cover more than 20 % of the vessel's cross-sectional area so that air movement (convection) within the vessel shall not be restricted during the test.

7.3 Glass dish, consisting of a petri or other shallow dish approximately 150 mm in diameter to hold powdered sulfur. The dish may be supported above the constant-humidity solution with plastic blocks or floated on the liquid. The free space of the liquid surface shall be large enough to guarantee equilibrium conditions in the test vessel for the entire test period.

7.4 Air-circulating oven, capable of maintaining the test vessel at a temperature of $50^\circ\text{C} \pm 2^\circ\text{C}$.

7.5 Thermometer or other temperature sensor, having a range of at least $40^\circ\text{C} \pm 1^\circ\text{C}$ to $60^\circ\text{C} \pm 1^\circ\text{C}$, which can be kept in the test vessel during the test.

7.6 Dielectric-detector hygrometer, with a remote sensor probe that can be placed in the test vessel, for the range of 75 % to 95 % RH.

7.7 Optical stereomicroscope, magnification $\times 10$. One eyepiece should preferably contain a graduated reticule for measuring the diameter of tarnish spots. If fitted, the reticule shall be calibrated for the magnification at which the microscope is to be used.

7.8 Light source, incandescent or circular fluorescent.

8 Test specimen preparation

Avoid any unnecessary handling of the specimens, and then handle only with tweezers, microscope lens tissue or clean, soft cotton or nylon gloves.

Prior to the test, inspect the sample at $\times 10$ magnification under the stereomicroscope (7.7) for any evidence of particulate matter. If present, the particles shall be removed by dusting with clean, oil-free air. Then, thoroughly clean the particle-free samples by gently rinsing with solvents or solutions that do not contain CFCs, chlorinated hydrocarbons or other known ozone-destroying compounds, and air-dry with clean air. A hot, analytical-reagent-grade methanol, ethanol, denatured ethanol or isopropanol dip is often useful in speeding up the drying.

The following procedure has been found to be useful in avoiding the use of chlorinated hydrocarbons:

- Keep individual specimens separated if there is a possibility of damage to the measurement area during the various cleaning steps.
- Clean the specimens for 5 min in an ultrasonic cleaner which contains a hot ($65\text{ }^{\circ}\text{C}$ to $85\text{ }^{\circ}\text{C}$) 2 % aqueous solution of a mildly alkaline (pH 7,5 to 10) detergent.
- After ultrasonic cleaning, rinse thoroughly under warm running tap water for at least 5 s.
- Rinse ultrasonically for 2 min in fresh distilled or deionized water (see 6.1) to remove the last detergent residues.
- Immerse in fresh analytical-reagent-grade methanol, ethanol, denatured ethanol or isopropanol, and ultrasonically "agitate" for at least 30 s in order to remove the water from the specimens.
- Remove and air-dry specimens until the alcohol has completely evaporated. If an air-dusting is used as an aid to drying, the air shall be oil-free, clean and dry.
- Do not touch the measurement area of the specimens with bare fingers after cleaning.

Re-inspect samples under $\times 10$ magnification for particulate matter on the surface. If particles are found, repeat the cleaning step. Surface cleanliness is extremely important. Contaminants, such as plating salts and flakes of metal, may give erroneous indications of porosity.

Omit the cleaning steps for samples having tarnish-inhibiting or lubricant coatings, or both, if it is desired to determine the efficiency of the coating in the reduced-sulfur atmosphere.

For nominal porosity-testing purposes, prepare the specimens so that the measurement areas (i.e. the significant surfaces) have optimum exposure to the test environment.

9 Procedure

9.1 Test vessel equilibration

For the initial operation of the apparatus, prepare the test vessel (7.1) for equilibration for at least a 24 h period before the first specimen exposure.

NOTE — For all subsequent tests, the initial 24 h equilibration procedure does not have to be repeated, [see also last paragraph in this subclause and subclause 9.2, item e)].

- Place the test vessel in the oven (7.4) with the sample support (7.2) in place. Place the saturated solution of potassium nitrate (6.2) in the bottom of the vessel. To ensure that the solution remains saturated at 50 °C, add approximately 20 g/100 ml of additional potassium nitrate crystals to the solution at room temperature.
- Place the lid on vessel (do not seal it with grease), insert the thermometer or other temperature sensor (7.5) and the remote humidity probe (7.6) through the opening in the top of the lid (leave the stopper out), and set the oven control to 55 °C.
- During equilibration, open the vessel occasionally and stir the contents. As the temperature in the vessel approaches 50 °C, as indicated by the temperature probe, adjust the oven temperature as needed to stabilize the vessel at 50 °C. Do not close the vent in the stopper as this may cause the relative humidity to approach 100 %.
- Fill the glass dish (7.3) half-full with sulfur (6.3) (break up any large lumps), and place the dish on supports above the potassium nitrate solution or float the dish directly on the solution (see figure 1).
- Replace the lid and insert the vented stopper in the lid opening. Monitor the vessel temperature over several hours, and adjust the oven temperature as needed to keep the vessel at 50 °C $\pm$ 2 °C. When stability has been attained, and the relative humidity is in the 85 % to 90 % range, the apparatus is ready for insertion of the specimens.

The system described in this section, may be reused for many subsequent tests without replacing the chemicals, and will remain stable for up to 6 months as long as the chemicals do not become contaminated with corrosion products or dirt. If allowed to cool, the potassium nitrate mixture will solidify, but it will liquefy again when the vessel is reheated and the solution stirred. Break up crusts and lumps of hardened potassium nitrate and stir into the slurry. Add a few millilitres of water (see 6.1) if necessary to return the solution to its original condition.

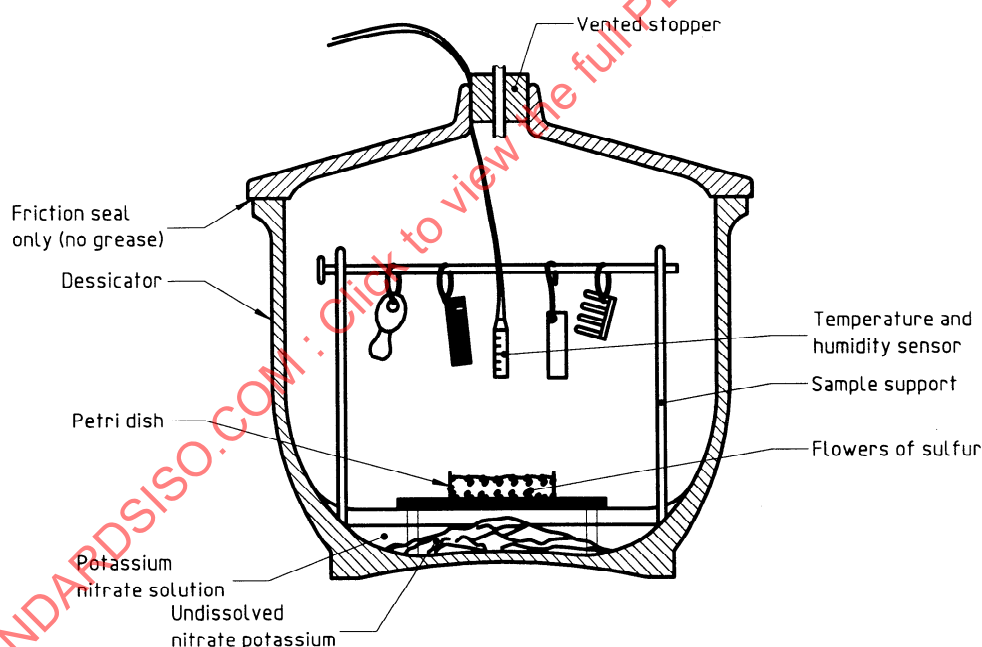


Figure 1 — Typical test equipment arrangement

9.2 Test procedure

Bring the test vessel to equilibrium as described in 9.1. Place the clean specimens in the test vessel as rapidly as possible so as to minimize deviations from equilibrium conditions. Also place a clean, unplated copper or copper-alloy panel in the vessel each time a test is run to act as an internal control, that is to show that the test system is operative. The copper should start to darken within a few hours.

- During the first 1 h to 2 h of the test run, leave the vessel slightly open, by removing the vented stopper, in order to prevent moisture condensation while the system is coming to the test temperature. When the test temperature is reached and the relative humidity is in the 85 % to 90 % range (which may take 1 h to 2 h), replace the vented stopper.

- b) During the first 2 h to 3 h of exposure, check the temperature and humidity in the desiccator and record it at suitable intervals in order to ensure the attainment of equilibrium conditions. Do the same towards the end of the test.
- c) Continue the test for the required time; this shall be 24 h, unless otherwise specified. The test system may be left overnight (or over the weekend for a 3-day test) without further monitoring.
- d) At the end of the test, remove the specimens, replace the vessel lid and allow the specimens to cool to room temperature before examining them.
- e) For all subsequent runs, the operations described in 9.1 may be eliminated. However, routine checks of the actual temperature and humidity within the vessel shall still be made, and occasional stirring of the potassium nitrate solution may be required before a new run.

10 Examination and evaluation of specimens

Examine the measurement areas at $\times 10$ magnification under the stereomicroscope (7.7), using the light source (7.8).

- a) The presence of brown or black tarnish marks or spots indicates that the finish is porous at these sites down to the copper, copper-alloy or silver substrate. This tarnish tends to creep from the pores and enlarge the marks or spots over the test period.
- b) If the pore sites are to be counted, the following hints may be useful as an aid to counting:
 - 1) Count only tarnish and corrosion products that are brown to black.
 - 2) Do not consider loose contamination that can easily be removed by mild air-dusting as tarnish or corrosion products.
 - 3) Move the specimen around under the light to vary the angle to verify pore indications. Burnished gold can give the appearance of black spots.
- c) Measure and count a tarnish or corrosion mark or spot when at least three-quarters of the spot falls within the measurement area. Tarnish creepage films which start outside the measurement area but fall within it, shall not be counted. However, the presence of significant tarnish creepage shall be recorded and its location given.
- d) Pore size shall be defined by the longest diameter of the corrosion product. Unless otherwise specified, corrosion products smaller than 0,05 mm in diameter shall not be counted. A graduated reticule in the microscope eyepiece is useful as an aid to counting and sizing.

NOTE — A useful sizing technique is to tabulate the pores in accordance with three size ranges: These are approximately

- a) 0,12 mm diameter or less;
 - b) between 0,12 mm and 0,4 mm diameter;
 - c) greater than 0,4 mm diameter.
- e) The acceptable number, size and location of these tarnish or corrosion marks or spots shall be as specified in the appropriate drawing or specification.

Annex A

(informative)

Significance and use

A.1 Coating quality

A major use of this test procedure is for determining coating quality. Porosity tests are indications of the completeness of protection or coverage offered by the coatings, since the coatings described in clause 1 are intended to be protective. The porosity test results are, therefore, a measure of the deposition process control.

A.2 Application to underplate quality

A particular purpose of the humid sulfur vapour test is for determining the quality of underplates of nickel or nickel alloy in those finish systems that have thin (1 μm to 2 μm or less) top layers above the nickel, since porosity in the underplate usually continues into such top layers.

A.3 Application to indoor environmental tarnishing

The humid sulfur vapour test is often used as an environmental test to simulate many indoor humid atmosphere tarnishing and tarnish creepage effects. However, the chemistry and properties of these tarnish films may not resemble those found in other service environments. For such product performance evaluations, the test should only be used in combination with other performance evaluation tests, as specified in the referencing document for that product.

A.4 Relationship to ageing tests

Porosity tests differ from corrosion and ageing tests, since the latter are intended to measure the chemical inertness of the coating. In contrast, in a good porosity test procedure, the corrosive agent should not attack the coating. It must, instead, clean, depolarize and/or activate the substrate metal exposed by the pore, and attack it sufficiently to cause reaction products to fill the pore to the surface of the coating.

A.5 Sensitivity

The humid-sulfur test is highly sensitive, and is capable of detecting virtually all porosity that penetrates down to copper or copper alloys. Since nickel is not attacked by moist sulfur vapour at 100 °C or less, this test cannot be used to detect pores or cracks in the top coating if such pores or cracks do not penetrate through the nickel underplate overlying the copper.

A.6 Tolerable porosity

The level of porosity in the coating that may be tolerable depends upon the severity of the environment that the product is likely to encounter during service or storage. Also, the location of the pores on the surface is important. If the pores are few in number or away from the significant surfaces, their presence can often be tolerated.