BS ISO 18929:2012

BSI Standards Publication

Imaging materials — Wet-processed silver-gelatin type black-and-white photographic reflection prints — Specifications for dark storage

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National foreword

This British Standard is the UK implementation of ISO 18929:2012. It supersedes BS ISO 18929:2003 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CPW/42, Photography.

A list of organizations represented on this committee can be obtained on request to its secretary.

ISBN 978 0 580 75883 6

ICS 37.040.20

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 April 2012.

Amendments issued since publication

Date	Text affected

INTERNATIONAL
STANDARD

ISO
18929

Second edition
2012-04-01

Imaging materials — Wet-processed silver-gelatin type black-and-white photographic reflection prints — Specifications for dark storage

Matériaux pour l'image — Tirages photographiques par réflexion par traitement humide gélatinoargentique de type noir et blanc — Spécifications pour le stockage dans l'obscurité

Reference number
ISO 18929:2012(E)

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Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 18929 was prepared by Technical Committee ISO/TC 42, *Photography*.

This second edition cancels and replaces the first edition (ISO 18929:2003), which has been technically revised.

Introduction

Black-and-white silver-gelatin fibre-base papers have been important imaging materials for well over 100 years. Reflection prints, made with such papers, have become increasingly important pictorial and documentary records that are housed in many libraries, archives, museums, universities and other public and private institutions. Although the intrinsic stability of properly processed and stored silver-gelatin prints is very good, there are internal and external factors that can cause degradation of such prints during storage and shorten their useful life. This International Standard provides specifications for tests that evaluate the stability of black-and-white silver-gelatin prints under prescribed storage conditions. It does not cover tests for the possible harmful effects of extended exposure to light.

Black-and-white prints are laminates, whose main components are a paper base, a white opaque intermediate layer, an image layer, and a protective layer. Paper has been used as a support for prints since about 1840. The history of its evolution into a very stable, high alpha-cellulose type fibre-base in the 1920s and to a polyethylene resin-coated (RC) paper base in the 1960s has been covered extensively in the literature (see References [11], [12], [13], [14] and [15]).

The intermediate, white opaque layer can be of two types. For fibre paper, since the 1880s it has been a gelatin layer containing white barium sulfate pigment (baryta layer) and other additives that enhance the paper's reflectivity, hardness, holdout, adhesion and surface characteristics (glossy, matte, textured). The second type came into use in the 1960s with the introduction of an RC base. This has a paper core coated on both sides with water-impermeable extruded polyethylene layers. The top layer contains white titanium dioxide pigment that provides higher reflectivity than barium sulfate; the bottom layer is transparent and formulated to counteract the curl induced by the emulsion, which is coated on top of the pigmented layer.

Prints on fibre paper have the advantage of having demonstrated long-term stability from years of practical experience in both dark storage and in reasonable display conditions. Proper processing and cleanliness or lack of contamination are important. Diluted toning solutions have been used successfully to enhance stability (see Annex A).

Prints on an RC paper base offer the advantages of higher wet strength, reduction in washing and drying times, lower consumption of processing chemicals, better dimensional stability, lower curl, and freedom from cockle and other effects of differential shrinkage. As with fibre-base materials, toning has been used successfully to enhance stability. However, they can suffer from stability-related problems such as light-induced image discolouration, silver mirroring, yellowing and cracking of the polyethylene layer (see References [16], [17], [18] and [19]).

This International Standard only applies to prints in dark storage since an applicable test for light-induced image deterioration has not been agreed upon. One reason for this has been that different brands of RC papers, or papers manufactured at different periods, have exhibited widely varying stability characteristics. It has been very difficult to reconcile all of the observed differences in behaviour in a relatively simple standardized test (see Annex B).

The image layer of most black-and-white prints is a gelatin coating containing a dispersion of light-sensitive silver halide crystals that are selectively converted into metallic silver grains by an image-forming exposure and chemical processing. Gelatin is a natural polymer that has been the preferred binder for photographic materials since the 1880s because it has proven to be the best protective colloid for the precipitation, growth and controlled suspension of silver crystals and for the formation of a dry, flexible image layer during a subsequent coating operation. Gelatin also can be hardened to reduce its swelling and susceptibility to physical damage, without blocking the absorption and desorption of aqueous processing solutions required for image formation and removal or stabilization of chemical by-products (see References [20] and [21]).

Converting the metallic silver to a complex or pre-oxidized form of silver will improve image stability. Many toner solutions have been designed to accomplish this, such as selenium, sepia, gold, brown and poly-toners. For example, in the case of sepia toner treatment, the silver is converted from oxidizable metallic silver to a stable silver sulfide.

The storage stability and useful life of reflection black-and-white prints depends on their physical and chemical properties, as well as on the conditions under which they are stored. For many years, the term "archival medium" was used to designate a recording material that can be expected to retain information forever so that it can be retrieved without significant loss when properly stored. However, there is no such material and it is a term no longer employed for material or systems specifications of International Standards. Another reason for abandonment of the term is the multiplicity of meanings that it acquired over the years, ranging from “preserving information forever” to “temporary storage of actively used information”. The unambiguous term used in this International Standard is “life expectancy” (LE), defined as the length of time that information is predicted to be retrievable in a system after storage. For example, a designation of LE-100 indicates that the information can be retrieved without significant loss after at least 100 years. Reflection prints are classified according to their LE designation in this International Standard.

Imaging materials — Wet-processed silver-gelatin type black-and-white photographic reflection prints — Specifications for dark storage

1 Scope

This International Standard establishes the specifications for silver-gelatin photographic reflection prints intended for dark storage. It covers silver-gelatin print types of all weights.

This International Standard applies to wet-processed black-and-white silver-gelatin photographic prints, including those that have been chemically treated (with a gold, selenium, sulfur, or other chemical treatment bath) to improve the permanence of the silver image. It also applies to silver-gelatin prints processed by a monobath, which includes thiosulfate as a fixing agent followed by a conventional wash.

This International Standard is not applicable to instant black-and-white photographic prints, stabilization-processed black-and-white prints (those where the undeveloped silver halide has been chemically converted and not removed), or thermally processed black-and-white prints. It does not apply to colour or dye-based photographic prints, nor to prints that have been processed by a monobath using other than a thiosulfate-type fixing solution, or prints where the silver salts are rendered more soluble by means other than thiosulfate.

Laminated and adhesive mounted reflection prints, prints on poly (ethylene terephthalate) support, and prints that have been displayed are also excluded from this International Standard.

2 Normative references

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

ISO 5-3, *Photography and graphic technology — Density measurements — Part 3: Spectral conditions*

ISO 5-4, *Photography and graphic technology — Density measurements — Part 4: Geometric conditions for reflection density*

ISO 18907, *Imaging materials — Photographic films and papers — Wedge test for brittleness*

ISO 18917, *Photography — Determination of residual thiosulfate and other related chemicals in processed photographic materials — Methods using iodine-amylose, methylene blue and silver sulfide*

TAPPI T494 om, *Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus)*

3 Terms and definitions

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

3.1
archival medium
material that can be expected to preserve images forever, so that such images can be retrieved without significant loss when properly stored

NOTE As no such material exists, this is a deprecated term and as such is not to be used in International Standards for imaging materials or system specifications.

3.2
emulsion
image or image-forming layer(s) of silver halide photographic films, papers, and plates

3.3
life expectancy
LE
rating for the life expectancy of recording materials and associated retrieval systems

NOTE 1 The number following the LE symbol is a prediction of the minimum life expectancy in years for which information can be retrieved without significant loss when stored in the conditions defined in the relevant standards. For example, LE-100 indicates that the information can be retrieved after at least 100 years storage.

NOTE 2 The actual useful life of black-and-white paper is very dependent upon the existing storage conditions (see ISO 18902 and ISO 18920).

3.4
reflection print support
white, opaque support for the image-forming and auxiliary layers of a photographic print, intended for viewing by reflected light

3.5
treated silver image
silver image that has been given a specific treatment, either during or after processing, to modify colour or increase stability

4 Safety and operational precautions

4.1 Hazard warnings

Some of the chemicals specified in the test procedures are caustic, toxic, or otherwise hazardous. Safe laboratory practice for the handling of chemicals requires the use of safety glasses or goggles, and in some cases other protective apparel, such as rubber gloves, face masks and aprons. Specific danger notices are given in the text and footnotes for particularly dangerous materials, but normal precautions are required during the performance of any chemical procedure at all times.

The first time that a hazardous material is noted in the procedures, the hazard will be indicated by the word "DANGER" followed by a symbol consisting of angle brackets "〈 〉" containing a letter that designates the specific hazard. A double bracket "《 》" will be used for particularly perilous situations. In subsequent statements involving handling of these hazardous materials, only the hazard symbol consisting of the brackets and letter(s) will be displayed. Furthermore, for a given material, the hazard symbols will be used only once in a single paragraph.

Hazard warning symbols will not be used for common organic solvents when used in quantities of less than 1 litre, unless they are particularly hazardous.

Detailed warnings for handling chemicals and their diluted solutions are beyond the scope of this International Standard.

Employers shall provide training and health and safety information in conformance with legal requirements.

The hazard code system used in this International Standard is intended to provide information to the users and is not meant for compliance with any legal requirements for labelling, as these vary from country to country.

It is strongly recommended that anyone using these chemicals obtains pertinent information from the manufacturer about the hazards, handling, use and disposal of these chemicals.

4.2 Hazard information code system

〈B〉 Harmful if inhaled. Avoid breathing dust, vapour, mist or gas. Use only with adequate ventilation.

〈C〉 Harmful if contact occurs. Avoid contact with eyes, skin or clothing. Wash thoroughly after handling.

⟨F⟩ Will burn. Keep away from heat, sparks and open flame. Use with adequate ventilation.

⟨O⟩ Oxidizer. Contact with other material may cause fire. Do not store near combustible materials.

⟨S⟩ Harmful if swallowed. Wash thoroughly after handling. If swallowed, obtain medical attention immediately.

⟨⟨S⟩⟩ May be fatal if swallowed. If swallowed, obtain medical attention immediately.

4.3 Safety precautions

4.3.1 All pipette operations shall be performed with a pipette bulb or plunger pipette. Failure to observe this warning notice can result in cyanide poisoning. This is a critical safety warning.

4.3.2 Digestion procedures shall be performed in an exhaust hood. Hydrogen cyanide or other toxic substances can be evolved.

4.3.3 Safety glasses shall be worn for all laboratory work.

4.3.4 Cyanogen iodide (CNI) may be detoxified by treatment with sodium hypochlorite.

5 Requirements for physical stability of prints

5.1 Wedge brittleness

Unincubated RC paper shall not show a paper crack value greater than 12 mm when tested as described in 8.1.4. Incubated RC paper shall not show an increase in the paper crack value greater than 14 mm when incubated as described in 8.1.2 and tested as described in 8.1.4.

The test is not run on unincubated fibre paper. Incubated fibre paper shall not show a crack value greater than 14 mm when incubated as described in 8.1.2 and tested as described in 8.1.4.

5.2 Tensile energy absorption (see Annex C)

Fibre paper and RC paper shall not show a decrease in tensile energy absorption (TEA) greater than 50 % when incubated as described in 8.2.2 and tested as described in 8.2.4.

5.3 Resin cracking of RC papers (see Annex D)

After 30 days, processed RC papers shall not show any evidence of resin cracking when tested as described in 8.6.5.

6 Requirements for processed image stability (see Annex E)

6.1 Residual thiosulfate concentration

Prints shall be fixed in solutions containing either sodium thiosulfate (hypo) or ammonium thiosulfate. After processing, fibre-base and RC-base black-and-white prints shall not contain more than 0,014 g/m^2 of residual thiosulfate [calculated as thiosulfate ions ($S_2O_3^{2-}$) when measured by the iodine amylose method in ISO 18917].

NOTE 1 The concentration of thiosulfate is expressed in grams per square metre (g/m^2), which conforms to SI units.

NOTE 2 0,010 g/m^2 = 1 µg/cm^2.

NOTE 3 A very low concentration of thiosulfate due to excessive washing may cause the silver image to be more susceptible to oxidative attack. These concentrations may be below the detection limit of ISO 18917.

Three methods for measuring residual thiosulfate levels are described in ISO 18917, i.e. the iodine amylose, methylene blue, and silver sulfide densitometric test methods. All of them are considered sufficiently reliable to determine thiosulfate concentrations at the 0,014 g/m^2 level, but only the iodine amylose method has been found to give reliable results with all types of fibre-base and RC prints. Therefore, it is the only method chosen for this International Standard.

The iodine amylose method measures only the concentration of thiosulfate ions. It can be run up to two weeks after processing, but the analysis shall be carried out with eluent obtained from a minimum density area of the processed print. It is only in such areas that the thiosulfate concentration does not change appreciably over a two-week period.

The methylene blue method shall not be used because it fails to detect residual thiosulfate in RC-base prints whose unexposed emulsion layers contain a considerable amount of developing agent in order to provide very rapid development during processing.

While the silver sulfide method does detect residual thiosulfate in RC-base prints, it also measures the concentration of polythionate decomposition products and other residual chemicals. Moreover, it also has been shown to give exaggeratedly high thiosulfate values with some RC prints (see Reference [22]).

Hypo-eliminating agents containing strongly oxidizing substances, such as peroxides or hypochlorites, shall not be used because they contain peroxides that attack the silver image (see Annexes E and F). However, the use of hypo-clearing solutions (such as a 2 % solution of sodium sulfite containing a wetting agent) does facilitate the washing of thiosulfate ions from the fibre prints without chemically altering the thiosulfate. They should not be used for RC prints.

6.2 Residual silver concentration

The processed print shall not contain more than 0,025 g/m^2 of silver when tested in accordance with 8.4.3 or 8.5.3 using the atomic absorption technique.

6.3 Yellowing limit (see Annex G)

The status A blue density of minimum density areas shall not increase by more than 0,08 units on the front (emulsion) surface or the back surface of the prints after incubation under conditions specified in 8.3.2 and testing as described in 8.3.3.

7 LE designation

Prints that meet all the specifications set forth in this International Standard shall have an LE rating of 100.

8 Test methods

8.1 Wedge brittleness

8.1.1 Preparation of specimens

Paper samples shall be exposed and processed to yield maximum density. Specimens shall be cut in an atmosphere of (23 ± 2) °C and (50 ± 5) % RH. The cutter shall be of a precision type and shall provide specimen edges that are smooth and free of nicks. Specimens shall be 300 mm long by 15 mm to 16 mm wide.

A set of 10 specimens shall be prepared for the original measurements and another set of 10 specimens for incubation as described in 8.1.2. The operator in handling the specimens, both in their preparation and testing, shall wear moisture-impermeable dust- and powder-free gloves.

NOTE Latex gloves can cause hypersensitivity in some individuals.

8.1.2 Incubation

One set of 10 specimens shall be freely suspended for 30 days in a forced-air oven maintained at (80 ± 2) °C and (50 ± 2) % RH. The short-term fluctuation in relative humidity shall not exceed ± 5 % RH.

8.1.3 Conditioning of specimens

Specimens shall be conditioned at (23 ± 1) °C and (20 ± 2) % RH before measurements. Fibre papers shall be conditioned for at least 1 day and RC papers for at least 7 days prior to measurement. The specimens shall be conditioned in racks that permit free circulation of air around the specimens.

8.1.4 Measurement

Specimens shall be tested at (23 ± 1) °C and (20 ± 2) % RH, as described in ISO 18907, using wedge apparatus with a 74 mm opening.

8.1.5 Reporting

Specimens shall be evaluated for either paper cracks or paper breaks, depending on which occurs at the wider wedge opening. Specimens which pass through the narrowest point of the wedge (1,5 mm) without failure shall be arbitrarily assigned a value of 1,0 mm, to permit averaging with those specimens which show failure caused by paper cracks or paper breaks.

The average of 10 specimens shall be calculated for both unincubated and incubated specimens. Samples shall meet the criteria given in 5.1.

NOTE Paper cracks may be evident by white paper fibres showing through the emulsion layer processed to maximum density.

8.2 Tensile energy absorption

8.2.1 Preparation of specimens

Paper specimens shall be prepared as described in 8.1.1. A set of 20 specimens shall be prepared for the original measurements and another set of 20 specimens for incubation as described in 8.2.2.

8.2.2 Incubation

One set of 20 specimens shall be hung freely in a controlled forced-air oven maintained at (80 ± 2) °C and (50 ± 2) % RH for 30 days. The set-point accuracy for the RH shall be as described in 8.1.2.

8.2.3 Conditioning

Specimens shall be conditioned as in 8.1.3.

8.2.4 Measurement

Specimens shall be tested at (23 ± 1) °C and (50 ± 2) % RH for tensile energy absorption (TEA) as described in TAPPI T494 om.

8.2.5 Reporting

The average TEA of 20 specimens shall be calculated for both unincubated and incubated specimens. Samples shall meet the specification given in 5.2.

Attention shall be given to the sections of TAPPI T494 om which pertain to the discarding of tensile measurements.

8.3 Yellowing

8.3.1 Preparation of specimens

Two minimum density specimens shall be prepared for each sample and conditioned as outlined in 8.1.3. The area of each specimen shall be at least 90 cm^2. To prevent contamination by fingerprints, the operator shall wear gloves during the preparation and testing of the specimens.

8.3.2 Incubation

Both specimens shall be freely suspended for 14 days in a forced-air oven maintained at (80 ± 2) °C and (50 ± 2) % RH. The short-term fluctuation in the test chamber shall not exceed ± 5 % RH.

8.3.3 Measurement

The status A blue reflection density of both specimens, backed by a black material, shall be measured before and after incubation (see Annex H). The spectral characteristics of the densitometer shall conform to ISO 5-3, and its geometry to ISO 5-4. Four measurements shall be made of the front and of the back surfaces of the two specimens, making a total of 16 measurements.

8.3.4 Reporting

The average of eight measurements shall be calculated for the front (emulsion) surface and the back surface, before and after incubation. The sample shall meet the density criteria specified in 6.3.

8.4 Residual silver compound test using cyanogen iodide (CNI) extraction

8.4.1 General

NOTE 1 For additional information, refer to References [7], [8], [9] and [10].

NOTE 2 The hazard rating for concentrated CNI solution is: (DANGER:⟪S⟫ ⟨B⟩ ⟨C⟩).

8.4.2 Specimen preparation

Two specimens of a processed print of at least 65 mm × 65 mm shall be tested. These specimens shall be taken from the end of the processing run and from a clean image-free (D_{min}) area of the print. The specimens shall not be blotted dry (this eliminates possible contamination from the blotter).

With a calibrated 60 mm diameter paper punch, a disc shall be punched from the clear area of the specimen and transferred into a 15 ml centrifuge tube. Then 5,00 ml ± 0,02 ml of 5 % CNI solution shall be pipetted into the tube, and the tube shall be capped and shaken in order to dislodge the specimen from the bottom of the tube. This is done to allow the 5 % CNI solution to fully cover both sides of the disc as the punched specimen will settle to the bottom of the tube. The 5 % CNI will extract silver from the specimen paper for 15 h (normally, samples are extracted overnight).

WARNING — CNI is a compound that shall be treated with extreme caution. When CNI is mixed with any form of acid, hydrogen cyanide, a deadly gas, is formed. Therefore, all sample preparation requiring CNI shall be done wearing gloves and in a fume hood.

When analysing the samples with CNI is finished, they shall be washed with distilled water under suction for at least 10 min. Special precautions are required for cleaning and disposal.

8.4.3 Analytical procedure

The specimens shall be analysed, along with a known silver-control standard solution such as NIST 3151[1], using an atomic absorption spectrophotometer at a wavelength of 328,1 nm.

NOTE NIST is the United States National Institute for Standards and Technology.

Flame ionization shall be performed using a burner with air and acetylene to produce a lean, blue flame at a sample flow rate of 5 ml/min. The samples shall be aspirated for 10 s, and then three consecutive absorbency readings of 5 s each shall be measured. The 5 % CNI blank solution shall be aspirated for at least 5 s between samples.

A dilution of the sample is necessary if the sample concentration exceeds the highest standard used for calibration. The sample shall be diluted to within the linear range.

The instrument shall be calibrated with the known concentration of silver standard solution before analysing the unknown specimens. Sample concentration values are obtained from a calibration plot of absorbance of the standard versus its concentration.

NOTE 1 The hazard code for silver nitrate is: (DANGER: ⟨C⟩ ⟨S⟩).

NOTE 2 An alternative procedure for those areas in which the use of CNI is environmentally precluded is given in 8.5.

8.4.4 Calculation

The concentration of silver in paper (c_{Ag}), expressed in grams per square metre, is given by the formula

$$c_{\text{Ag}} = \frac{(\rho_{\text{Ag}} - \rho_{\text{Ag,0}}) \cdot V \cdot d}{A \times 10^6}$$

where

ρ_{Ag} is the concentration of silver, in micrograms per millilitre (µg/ml), found in the sample solution;

$\rho_{\text{Ag,0}}$ is the concentration of silver, in micrograms per millilitre (µg/ml), found in the reagent blank 5 % CNI solution;

V is the volume, in millilitres (ml), of the sample solution;

d is the dilution factor (if necessary);

A is the area of the sample, in square metres (m^2), e.g. 0,002 83 m^2.

8.5 Residual silver compound test by use of sulfuric acid/nitric acid extraction

8.5.1 General

This alternative method is especially suitable for the analysis of silver in Europe or other countries where the use of CNI is environmentally prohibited. This method uses a microwave procedure that speeds up the digestion process to within a few minutes.

8.5.2 Experimental conditions and specimen preparation

Reagents: Milli-Q – water[2], H_2SO_4, CP (chemically pure) (DANGER: ⟨⟨C⟩⟩), HNO_3 (70 % CP) (DANGER: ⟨B⟩⟨C⟩⟨O⟩).

Glassware: 25 ml volumetric vessel, pipettes of 1 ml, 2 ml and 5 ml volume, and a microwave vessel of 100 ml volume.

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[1] NIST 3151 is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

[2] Milli-Q – water is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Instruments: Microwave destruction apparatus.

Microwave Program 12: 2 min 250 W; 1 min 0 W (zero watts, power off); 10 min 300 W; and 10 min cool down.

Microwave Program 2: 1 min 250 W; 1 min 0 W; 5 min 250 W; 5 min 400 W; 10 min 650 W; and 15 min cool down.

Specimen preparation and specimen size shall be the same as described in 8.4.2. To ensure full sample digestion, the specimens are treated in a microwave oven in the following 2-step procedure.

a) The specimen shall be immersed in a 100 ml microwave vessel containing 1 ml of H_2SO_4 (DANGER: ⟨⟨C⟩⟩) and Program 12 on the microwave shall be activated.

b) Upon completion of Program 12, 2,5 ml of HNO_3 (DANGER: ⟨B⟩⟨C⟩⟨O⟩) shall be added to the specimen vessel and Program 2 shall be started.

After cooling, the colourless and clear solution shall be transferred to a 25 ml volumetric flask with milli-Q – water. If the solutions are not clear, the whole procedure shall be repeated.

WARNING — Extreme care should be exercised during storage, handling and disposal of used pipettes, as sulfuric acid will react violently with water and the fumes of nitric acid cause oxidation.

8.5.3 Analytical procedure

The solution is added to a spectrophotometer or an ICP (inductively coupled plasma) atomic emission spectrophotometer.

The specimens shall be analysed, along with a known silver-control standard solution such as NIST 3151, using an ICP atomic emission spectrophotometer at a wavelength of 328,1 nm or an atomic absorption spectrophotometer at a wavelength of 328,1 nm.

8.5.4 Calculation

The concentration of silver in paper is obtained using the same formula as described in 8.4.4 by substituting the appropriate blank silver concentration ($\rho_{Ag,0}$) in the mixture of H_2SO_4 and HNO_3.

8.6 Resin cracking

8.6.1 General

Although this International Standard is for prints not intended for display, a light is used in this test to accelerate the occurrence of resin cracking. Resin cracking can occur in total darkness during periods of temperature and/or humidity fluctuation. In such cases, the emulsion is stressed, which can lead to resin cracks.

8.6.2 Purpose

This test measures the tendency of the resin layer in RC paper to degrade. It consists of exposing RC paper to fluorescent light at an elevated temperature and periodically subjecting the paper to thermal shock by lowering the temperature. The incubation time until resin cracking occurs is a measure of resin-layer stability.

8.6.3 Apparatus

A schematic view of the apparatus is shown in Figure 1. It consists of the following elements.

8.6.3.1 Forced-air oven, which can control the temperature at (80 ± 2) °C and the relative humidity at (50 ± 2) % RH. Air circulation should be sufficient to provide some air movement, but low enough not to disturb the specimens.

8.6.3.2 Film clips or brackets, to hold the specimens in a fixed plane.

8.6.3.3 Bank of cool-white fluorescent lamps, positioned so that the light intensity is 1 Klx (100 foot-candles) at the specimen plane.

8.6.3.4 Standard window-glass filter, 6,5mm, placed between the fluorescent lamps and the specimen plane.

NOTE Most bare-bulb fluorescent lamps have a strong ultraviolet (UV) emission at 313 nm that may unrealistically accelerate the degradation of the resin layer. Ordinary window glass does not transmit this emission.

8.6.4 Preparation of specimens

Paper specimens shall be processed to minimum density. A set of two specimens shall be prepared for each sample. Specimens shall be approximately 65 mm in length and 25 mm in width.

8.6.5 Procedure

Specimens shall be placed in the film clips (8.6.3.2) and inserted in the forced-air oven (8.6.3.1) with the emulsion surface facing the fluorescent lamps (8.6.3.3). The weight of any clamps should be sufficient to eliminate curl, but no greater. When the temperature of the oven has stabilized at (80 ± 2) °C, humidified air shall be introduced so that the relative humidity is at (50 ± 2) % RH.

NOTE 1 Humidified air is only allowed into the oven chamber after the temperature has reached the operating temperature in order to avoid moisture condensation on the specimens. Moisture condensation invalidates the test.

The fluorescent lights are turned on.

After 3 days and every 3 days thereafter, until 30 days have passed, the specimens shall be removed from the oven for evaluation. This shall be accomplished by first turning off the humidified air stream. Care shall be taken that the front (emulsion) surface of the specimens is protected from fingerprints and that the specimens are not flexed.

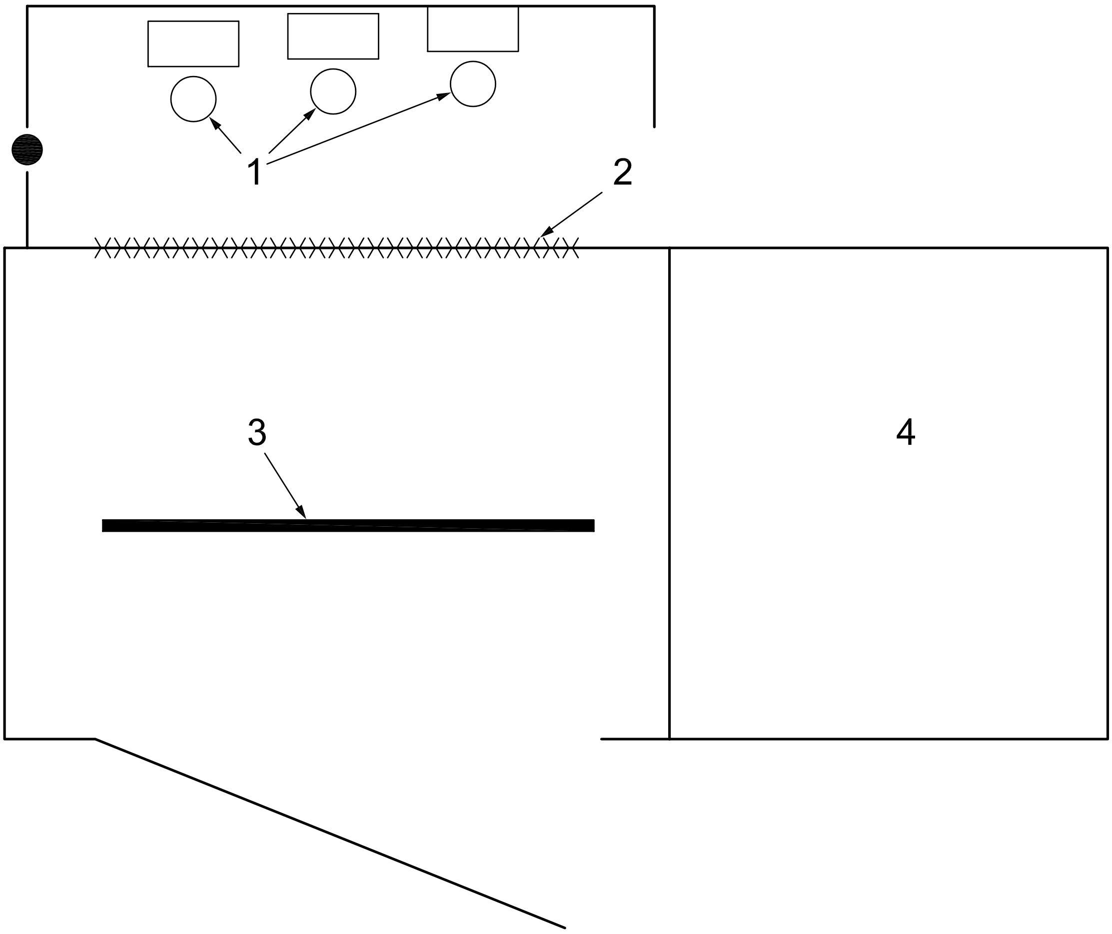
The front (emulsion) surface of the specimens shall be examined for resin cracks. This has occurred when a crack extends completely through the resin layer. Examination is facilitated using a magnifying glass and a low-angle, specular light source. Cracks near the clamped surface shall be ignored.

NOTE 2 Cracks can be confirmed by applying a small drop of alcohol and dye to the area. If a crack exists, the solution wicks into the paper base and is visible from the back surface.

After the specimens have been out of the oven chamber for 2 h, they are returned for subsequent incubations, following the procedure described above.

8.6.6 Reporting

The number of incubation days required to produce resin cracks shall be recorded. The samples shall meet the requirement given in 5.3.



Key

1	fluorescent lamp units
2	glass
3	sample plane
4	humidity-control unit

Figure 1 — Resin-cracking apparatus

Annex A
(informative)

Stabilization treatments to prevent silver oxidation

Silver images can be rendered more resistant to oxidation by partial or complete conversion into more stable compounds, notably silver sulfide and silver selenide, by protection of the silver surface with a layer of gold, or by use of SCN (thiocyanate). Such a “stabilizer treatment” has become a mandatory after-treatment of silver-gelatin images that are to have a long life expectancy under less-than-optimal storage conditions.

Suitable thiols, polysulfide and selenium toners are available in concentrated liquid form. Formulas for mixing gold toners are published in photographic textbooks.

ISO 18915 provides useful information on stabilization treatments. For additional information, see References [23], [24], [25] and [26].

Annex B
(informative)

Potential silver-image discolouration of RC prints under display conditions

NOTE For additional information on this subject, see References [16], [17], [18] and [19].

Some silver-gelatin prints on an RC-paper support are susceptible to a special variant of colloidal silver discolouration that involves exposure to intense light or ultraviolet (UV) radiation. Absorption of such radiant energy by the titanium dioxide pigment in the polyethylene layer below the emulsion causes the formation of titanium trioxide and singlet oxygen. The presence of singlet oxygen can enhance the rate of colloidal silver discolouration, when the RC-paper print is displayed in a glass-covered frame that prevents the escape of oxidizing agents.

Even under more favourable display conditions, colloidal silver formation can occur, depending on:

- the presence of effective anti-oxidants and other stabilizers in the print material;
- the chemicals and procedures used for print processing;
- the spectral distribution, intensity and exposure cycles of the absorbed radiation;
- the relative humidity and temperature in the display area.

Annex C
(informative)

Tensile energy absorption

Tensile energy absorption (TEA) is the work required to rupture paper under a tensile force. It is proportional to the tensile break strength and the tensile elongation at break. Since the latter is quite low for paper, TEA is a difficult measurement to make.

Laboratory testing by members of ISO/TC 42 has shown, however, that TEA is a much better predictor of paper ageing than other tensile properties. Samples of photographic papers were preconditioned at 21 °C and 50 % RH and then incubated at elevated temperatures (ranging from 22 °C to 90 °C) at 50 % RH. The decrease in TEA was obtained as a function of incubation time.

The effect of temperature on the time for a given percentage loss in TEA followed a modified Arrhenius relationship. This gave confidence that a high-temperature incubation test could be used as a predictor of storage temperature behaviour. It was on the basis of such experimental results that conditioning at 80 °C and 50 % RH for 30 days was chosen in this International Standard.

Annex D
(informative)

Environmental resin-cracking

Polyethylene plastics exhibit a brittle type of failure, called stress-cracking, which may occur over relatively long periods up to many years (see Reference [27]). When this happens, it is caused by tensile stresses substantially lower than those causing short-time rupture. Depending on the manner of its initiation, the resulting failure may be recognized as environmental, solvent, oxidative, thermal or fatigue. The resistance to stress-cracking increases as density decreases, molecular weight increases, molecular-weight distribution narrows, and temperature increases.

Stress-crack failure, accelerated by the presence of promoters such as an alcohol, soap or wetting agent, is called environmental stress-cracking (ESC). In the absence of stress, these agents have no discernible effect on the polymer surface. Solvents such as toluene, which swell the polymer, promote stress-cracking. Oxidation also causes degradation. Thermal cracking is a purely physical phenomenon that can occur in an inert atmosphere or a vacuum and is initiated within the polymer mass rather than on the surface. Fatigue cracking occurs if there is a constant stress at a level just below the short-time strength.

Environmental stress-crack failure is critical in low-density polyethylene (LDPE). As with brittleness, it is influenced by thermal history. These reactions can occur in unpigmented plastic and in the absence of light-induced oxidation reactions.

Annex E
(informative)

Effects of residual thiosulfate and silver in processed prints

Thiosulfates are imbibed from the fixing bath and should be removed during washing to the level specified in 6.1. Otherwise, the two following harmful changes are likely to occur:

a) yellow-brown discolouration of the image silver, due to formation of silver sulfite;

b) irretrievable loss of image density, due to oxidation of the silver sulfite to white and soluble silver sulfate, especially under high temperature and relative humidity conditions.

Another fixer-related cause of image discolouration is the retention of silver thiosulfate complexes, usually brought about by insufficient treatment time or use of an exhausted fixing solution. Retained silver complexes will break down rapidly to form silver sulfite, resulting in overall yellow-brown discolouration of the print, including the staining of white areas (the limits of permissible silver concentration in prints are specified in 6.2). However, prolonged fixation is also harmful for two reasons:

1) thiosulfate will attack and bleach the image silver;

2) with fibre-base prints, thiosulfates and silver thiosulfate complexes will diffuse into the paper fibres and become so strongly adsorbed that even prolonged washing will fail to dislodge them. In time, this will lead to discolouration for the stated reasons.

In order to attain proper fixation of prints, the silver content of the fixing bath should not be higher than the manufacturer’s recommendations, otherwise complexes will be formed that cannot be removed by normal washing. To avoid this potential problem, a two-bath fixing technique can be employed in which most of the silver halides are dissolved in the first bath and any remainders in the second. The first bath is discarded when it reaches the point of exhaustion and is replaced by the second. This cycle can be repeated several times. However, a maximum of five cycles is usually recommended to avoid problems with contamination, dilution, evaporation, sludges and slimes.

Thorough washing is the second important requirement for preventing print discolouration due to residual thiosulfate. It is achieved by using rapidly flowing, fresh water of 15 °C to 25 °C, or by successive immersion in five separate volumes of fresh water.

The recommended time of washing for fibre-base prints is 50 min to 60 min in running water. The required wash time for RC prints ranges from 20 s to 30 s with efficient, automatic processing machines, to 3 min with manual processing. Longer wash times are not recommended for RC prints because of edge penetration. In addition, it is possible to take the residual thiosulfate to zero with RC papers but that is not recommended. A slight residual is good for long-term keeping for RC and fibre-base papers. It is almost impossible to remove all the thiosulfate from fibre-base prints. Washing aids are not recommended for RC prints for this reason.

The effectiveness of washing of fibre-base prints can be increased by treatment in a solution of 1 % to 2 % sodium sulfite or other inert salts that will displace the thiosulfates. This treatment can be employed before washing or between split-washing periods. Other factors that influence the effectiveness of washing are:

- pH of the fixing solution (higher rate at pH values above 4,9 which is the iso-electric point of gelatin);
- use of acid, hardening, or neutral, non-hardening fixer (gelatin hardening and low pH reduce the rate);
- silver content of the fixing solution (lower rate as silver concentration increases);
- water hardness (less effective with soft than with hard water);
- water temperature (increases effectiveness with warmer temperatures due to increased diffusion rate);

- level of agitation (increased effectiveness due to decrease of stagnant water at the emulsion surface and, therefore, rate of removal of fixation by-products).

Annex F
(informative)

Degradation of silver images due to extraneous oxidation

The image elements of silver-gelatin prints consist of filamentary-silver aggregates that have a very large surface-to-volume ratio. This enhances their susceptibility to degradation by aggressive oxidizing chemicals. The initial step in such degradation is the oxidation of the elemental silver to silver ions. In the second step, these ions migrate and disperse in the gelatin layer. In the third step, the silver ions are reduced to silver atoms that recombine to form colloidal-silver particles or silver complexes.

Depending on the concentration of reactants, the number and aggregation of colloidal-silver particles, and the humidity and temperature of the print, three different forms of blemishes can be formed singularly or in combination.

- One is a mirror-like deposit near the surface of the image layer. It has a blue colour when viewed by reflected light and a yellow colour by transmitted light.
- Another is yellow or orange-brown discolouration of the image, either partial or complete.
- The third is spots, variously called red spots, microspots or redox blemishes, that have a ring-like structure.

The colour of these colloidal-silver deposits is the result of the scattering of short-wavelength light by the microscopic-silver particles that are about 15 times smaller than typical image-silver grains.

All silver images are susceptible to oxidation and formation of colloidal silver, but the degree of vulnerability varies considerably, depending mainly on the components of the photographic material, the size and morphology of the silver grains, the presence of stabilizers in the components of the photograph, the composition of processing solutions, and storage conditions.

Oxidizing gases that can cause severe discolouration, even in very low concentrations, are hydrogen peroxide, oxides of nitrogen, ozone, and automobile exhaust fumes. They are present in most industrial and large city atmospheres. Peroxide is also given off by wood and fresh oil-based paints and may be emitted by paper enclosures. Toner treatment of the silver image by converting the silver to the complex state will minimize the problem (as described in Annex A).

Annex G
(informative)

Discolouration of black-and-white photographic prints

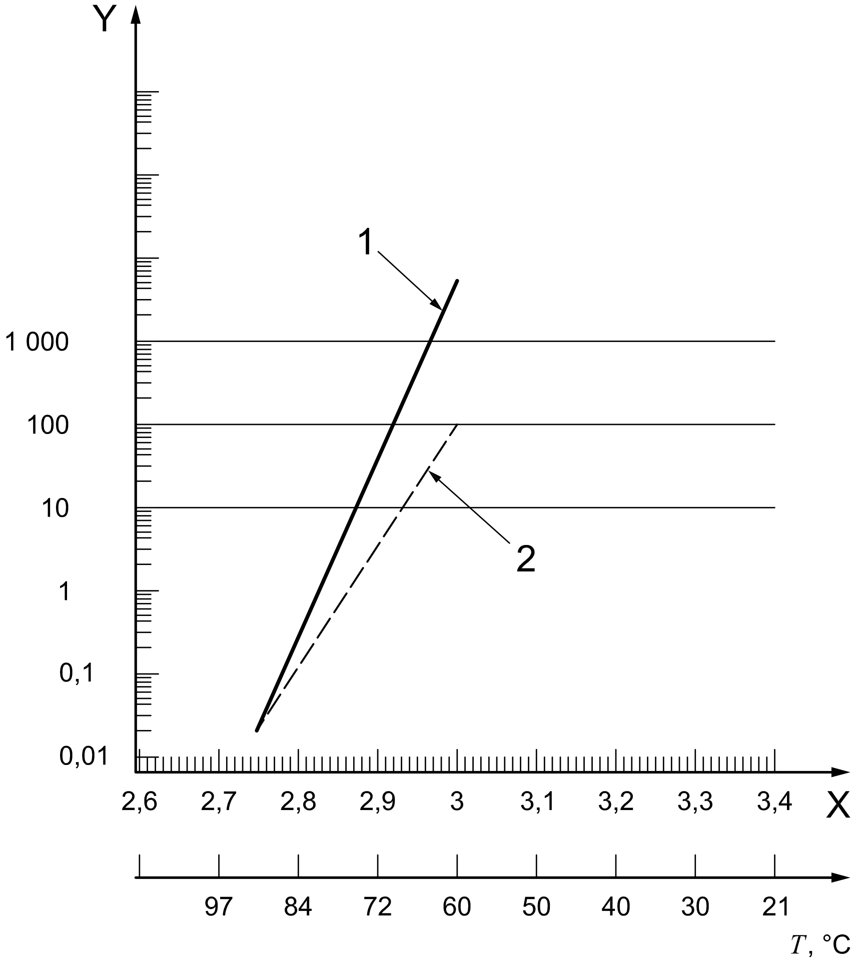
Reflection-type photographic prints tend to yellow with age, even when processed and stored in accordance with recommended practices, due to discolouration of various constituents, such as the cellulose fibres of the paper support, the gelatin emulsion, the white pigments and optical brighteners incorporated in the baryta layer of fibre papers or the resin layer of RC papers. This type of discolouration is more objectionable on the front surface than on the back surface of prints, because of its disproportionately large effect on the image quality of low-density areas.

In view of this fact, the end points of initial Arrhenius tests carried out to determine suitable limits of density changes were 0,05 for the front surface and 0,15 for the back surface.

Arrhenius plots obtained with these tests are shown in the composite graph of Figure G.1. It was evident from these results that thousands of years would be required for either surface to reach selected end points. Two conclusions were reached on the basis of these results:

- yellowing would not be a significant problem under recommended storage conditions;
- a single end point would be acceptable for front and back yellowing.

For additional information on the Arrhenius method, see ISO 18924.



Key

1 back

2 front

X 1 000 × (1/T °K) [plotted as the reciprocal of thermodynamic (absolute) temperature]

Y years for specified gain in D_{min}

Figure G.1 — Time versus temperature for a processed black-and-white photographic reflection print to show a status A blue density gain of 0,05 (front surface) or 0,15 (back surface)

Annex H
(informative)

Densitometric versus spectrophotometric measurement of yellowing

Status A blue densitometry has been chosen in this International Standard instead of spectrophotometry for yellowness evaluation, even though densitometric measurements do not provide full assessment of the contribution of the fluorescence of optical brighteners to the perceived whiteness of the D_{min} areas. The main reasons for this choice were as follows.

- In inter-laboratory tests, blue-filter densitometry was found to rank specimens in the same order for their whiteness as visual evaluation and spectrophotometry.
- Densitometry is well established throughout the photographic industry.
- The excitation of optical brighteners varies markedly with the ultraviolet (UV) content of the irradiation. Therefore, the perceived whiteness of prints containing optical brighteners varies with the spectral distribution of the illumination, being considerably greater in daylight than tungsten light. Similarly, the whiteness determined with a spectrophotometer (or colorimeter) depends on the spectral composition of the radiation incident on the specimen and on the sensor’s geometry and spatial response characteristics.

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