INTERNATIONAL STANDARD

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Photography — Methods for the evaluation of the effectiveness of chemical conversion of silver images against oxidation

Photographie — Méthodes d'évaluation de l'efficacité de la conversion chimique des images argentiques contre l'oxydation

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Contents

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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.

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 12206 was prepared by Technical Committee ISO/TC 42, *Photography*.

Annex A forms an integral part of this International Standard. Annexes B, C and D are for information only.

Introduction

Silver-gelatin photographs have been used extensively for recording and preserving information of lasting value in all fields of human activity. The long-term stability of these records has become of increasing concern in recent years, because image and support degradation have been found with accelerating frequency in photographic collections and archives.

ISO has published documents on various aspects of the stability and preservation of black-and-white silver-gelatin photographic materials. ISO 10602:1995, *Photography — Processed silver-gelatin type black-and-white film — Specifications for stability*, provides test methods and criteria for the physical properties, permissible residual processing chemicals, and the image quality of films. ISO 5466:1992, *Photography — Processed safety photographic films — Storage practices*, deals with the conditions required for maintaining and preserving the integrity of photographic films during storage. ISO 10214:1991, *Photography — Processed photographic materials — Filing enclosures for storage*, pertains to the materials used in contact with stored photographic materials.

If photographic film meets the material and processing specifications of ISO 10602 and is stored in accordance with ISO 5466 and ISO 10214, excellent stability will be obtained. Similarly, photographic paper prints should be stored in accordance with ISO 6051:1992, *Photography — Processed photographic paper prints — Storage practices*, and processed photographic plates in accordance with ISO 3897:1992, *Photography — Processed photographic plates — Storage practices*.

However, in practical situations it is not always possible to control the storage conditions, particularly with respect to contaminants.

Atmospheric pollutants such as peroxides, sulfur dioxide, ozone and nitrogen dioxide are very detrimental to silver images[1]. Such environmental pollutants are of increasing concern in our industrial society. They can cause oxidation of the silver with consequent silver migration. This results in image fading, silver mirroring and redox blemishes[2][3]. Oxidizing agents that diffuse out of enclosure materials cause similar defects.

Recent studies have shown that silver images can be made resistant to oxidizing pollutants by chemically treating the silver to form silver sulfide[4] or silver selenide[5], or by substitution of the silver by gold[6]. Such treatments are recommended when it is not possible to ensure the absence of contaminants, or when the importance of the image justifies the added expense.

This International Standard is an adjunct to the processing requirements and describes methods for evaluating the effectiveness of various treatments which impart greater stability to silver images.

Photography — Methods for the evaluation of the effectiveness of chemical conversion of silver images against oxidation

1 Scope

1.1 This International Standard describes methods for evaluating the effectiveness of chemical conversion treatments intended to increase the resistance of wet-processed silver images to oxidation. The treatment may be applied as part of the original processing, or it may be a post-processing treatment.

1.2 This International Standard applies to silver-gelatin images coated on to supports of either plastic, paper or glass.

1.3 It does not recommend general or specific treatments for silver images. Likewise, treatment temperature, times and replenishment rates are outside the scope of this International Standard. Factors to be considered in a stabilizing treatment are discussed in annex B.

1.4 This International Standard describes two test methods: the dichromate bleach test and the hydrogen peroxide incubation test[7]. The significance of each is discussed in annex C.

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 5-2:1991, *Photography — Density measurements — Part 2: Geometric conditions for transmission density.*

ISO 5-3:—[1], *Photography — Density measurements — Part 3: Spectral conditions.*

ISO 5-4:—[2], *Photography — Density measurements — Part 4: Geometric conditions for reflection density.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 treated silver images: Silver images that have been given a specific treatment, either during or after processing, to increase their stability.

3.2 toned silver images: Silver images that have been given a specific treatment, either during or after processing, to modify their colour.

4 Dichromate bleach test

4.1 Principle

This test consists of dissolving the treated silver image and measuring the retained density. This retained density is proportional to the silver that has been chemically converted to a non-bleachable compound, or has been substituted by a non-bleachable element.

1) To be published. (Revision of ISO 5-3:1984)

2) To be published. (Revision of ISO 5-4:1983)

4.2 Reagents

4.2.1 Bleach solution

A bleach solution shall be prepared by dissolving 90 g of anhydrous potassium dichromate in 1 litre of water. Subsequently, 96 ml of concentrated sulfuric acid shall be slowly added with constant stirring.

WARNING — Avoid contact with the eyes, skin and clothing. Wash thoroughly after handling. In case of contact, flush eyes and skin with water. Obtain medical attention immediately.

Take care to dispose of dichromate bleach solution in accordance with national and local hazardous waste disposal regulations.

4.2.2 Clearing solution

The clearing solution shall be prepared by dissolving 100 g of sodium sulfite in 1 litre of water.

4.3 Specimen preparation

Six uniform-density patches shall be prepared on the treated silver material with densities (D) ranging in approximately equal increments from 0,1 above D_{min} to D_{max}. The exact size of the patches is not critical, provided they cover the aperture of the densitometer and are easy to handle.

4.4 Procedure

Measure the treated silver image on the six uniform-density patches and on D_{min} for status A blue density. Densities shall be measured on a densitometer having spectral conformance to ISO 5-3. The densitometer shall have geometric conformance to ISO 5-2 for photographic films and plates, and geometric conformance to ISO 5-4 for photographic papers.

Then immerse the specimen in the bleach solution (4.2.1) for 30 s at (20 ± 5) °C, rinse it in water for 2 s, and clear for 30 s in the clearing solution (4.2.2). Then rinse the specimen in water, dry it and re-measure the status A blue density.

4.5 Calculation

The percent density retention is calculated by dividing the blue density after bleaching by the original blue density (after treatment but before bleaching) and multiplying by 100. Make this calculation for all six uniform-density patches.

With some photographic materials, particularly photographic paper prints, bleaching can cause an increase in the D_{min}. The percent density retention shall be corrected for any D_{min} increase, as shown in annex A.

4.6 Significance

The retained density is an approximation of the percentage of silver image that has been converted into substances which are not affected by oxidants or pollutants. A treatment which results in 65 % density retention or more after bleaching for all six density patches is considered a stable image[3].

5 Hydrogen peroxide incubation test

5.1 Principle

This test consists of exposing the treated silver images to hydrogen peroxide vapour and measuring the resultant change in density. A small change in density represents an image that is resistant to peroxides.

5.2 Reagents

5.2.1 Hydrogen peroxide, reagent grade, 2 % (*m/m*) solution, freshly prepared from a 30 % stock solution.

WARNING — Hydrogen peroxide is very corrosive. Caution should be used in handling hydrogen peroxide solutions. The stock solutions should be kept refrigerated in vertical vented bottles and kept away from combustibles. Gloves and protective clothing should be worn.

Take care to dispose of hydrogen peroxide solutions according to national and local waste disposal regulations.

5.2.2 Potassium chloride, saturated solution.

5.2.3 Potassium chloride, dry solid.

5.3 Apparatus

The components of the desiccator jar used to expose the test specimens to hydrogen peroxide vapour are

3) This density retention value is based on the fact that since two-thirds of the image will not be affected by oxidants, there would be no loss of information. Treatments which result in a lower percent density retention may also be very stable, depending upon the image density and the type of chemical conversion.

given in figure 1 and the assembled apparatus is shown in figure 2. It consists of the following elements.

5.3.1 Glass desiccator jar, having a nominal inside diameter of 150 mm and a capacity of 2 litres.

5.3.2 Ground plastic[4] desiccator lid, fitted with a fan.

The fan motor is attached to the top surface of the desiccator lid with the shaft going through the lid to the fan mounted on the inside surface. There shall be four fan blades, each approximately 25 mm in length. The fan shall rotate at approximately 2 000 r/min.

5.3.3 Plastic[4] collar, which shall fit snugly inside the desiccator on which the specimens are mounted.

The collar shall be roughly 80 mm in height with an inside diameter of 135 mm and a wall thickness of approximately 7 mm. The collar shall be fitted with three baffles, each approximately 80 mm in length, 20 mm in depth, and 25 mm in width[5]. A plan drawing of the collar and baffles is shown in figure 3.

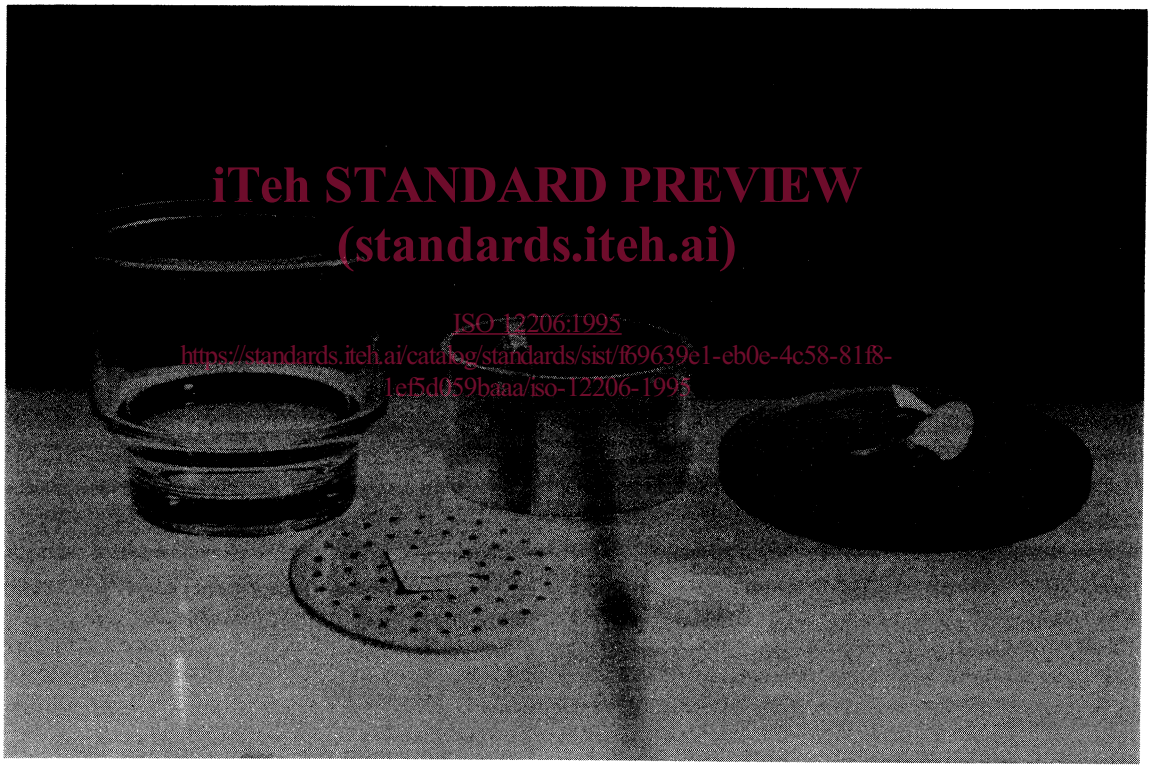

Figure 1 — Desiccator jar components

4) Poly(methyl methacrylate) has proved to be an acceptable plastic.

5) The baffles serve to provide more turbulent air movement and ensure uniform distribution of the hydrogen peroxide vapour. They may be constructed of a hydrogen-peroxide-resistant plastic, such as polycarbonate.

Figure 2 — Assembled desiccator jar

5.3.4 Perforated porcelain plate, of diameter 140 mm, which fits over the desiccator well.

5.3.5 Petri dish, of capacity 60 ml, which fits into the desiccator well and which holds a saturated salt solution to regulate the relative humidity.

5.3.6 Circular pad, approximately 40 mm in diameter, of 0,3 mm chromatography paper or filter paper[6], with a water flowrate of 100 mm to 150 mm per 30 min[7], which is wired to the upper side of the perforated porcelain plate with stainless steel wire.

5.3.7 Oven, fan-assisted, capable of being maintained at 50 °C ± 2 °C.

5.4 Specimen preparation

Six uniform-density patches shall be prepared with densities (D) ranging in approximately equal increments from 0,1 above D_{min} to D_{max}. The exact size of the patches is not critical, provided they cover the aperture of the densitometer and are easy to handle.

5.5 Procedure

5.5.1 Measure the status A blue density on the six uniform-density patches and on D_{min} before treatment. Densities shall be measured on a densitometer having spectral conformance to ISO 5-3. The densitometer shall have geometric conformance to ISO 5-2 for photographic films and plates and geometric conformance to ISO 5-4 for photographic papers.

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6) A suitable chromatography paper is Whatman No. 3 mm CHR paper. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

7) This refers to the capillary rise of water when the paper is partially immersed in water.

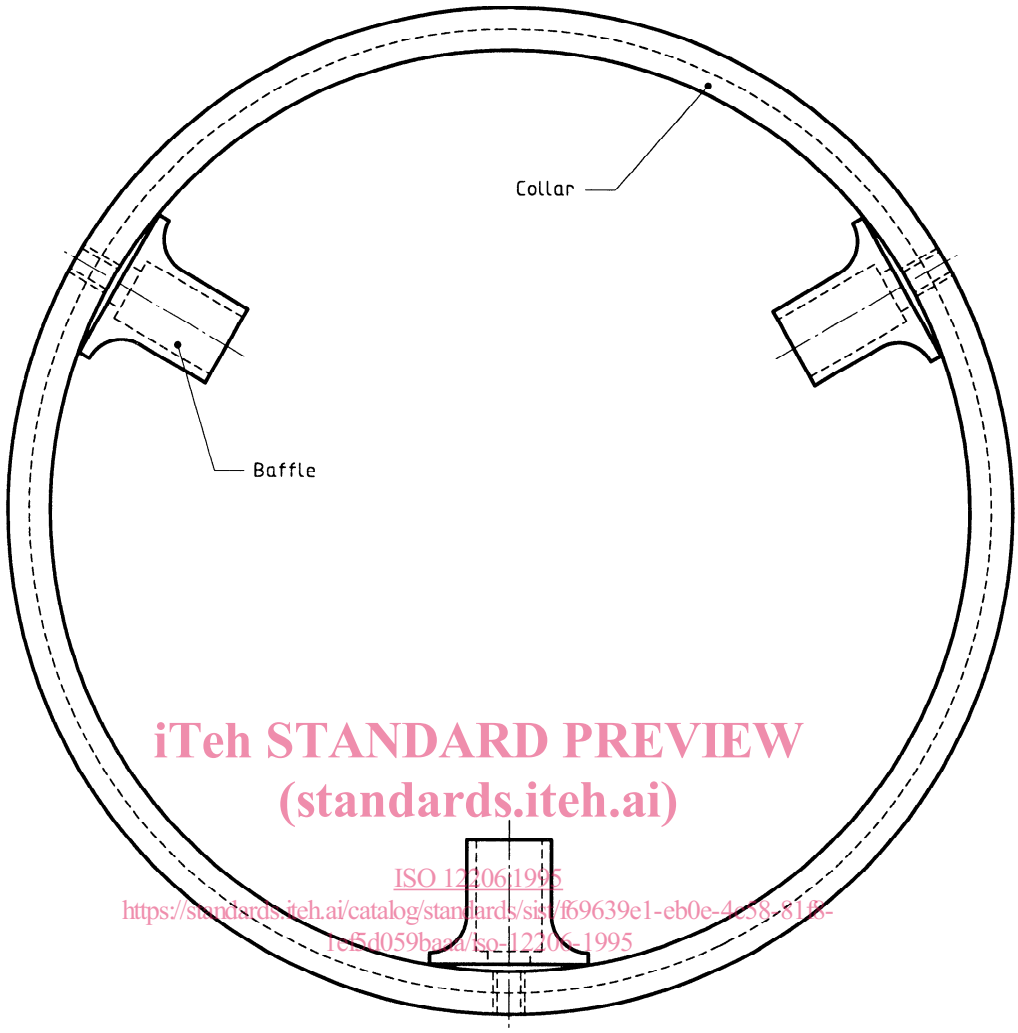

Figure 3 — Drawing of collar and baffles

5.5.2 Attach the specimens with the base side against the inside surface of the cylindrical collar[8]. Take care to ensure that the specimens are snug against the collar surface.

5.5.3 Place 5 ml of a saturated solution of potassium chloride (5.2.2) in the Petri dish (5.3.5) to achieve a relative humidity of 82 %. To maintain solution saturation, add 10 g of dry potassium chloride (5.2.3) to the Petri dish.

5.5.4 Charge the desiccator by the addition of 0,12 ml of the hydrogen peroxide solution (5.2.1) to the pad of chromatography paper (5.3.6). This gives a peroxide concentration of approximately 1 000 ppm.

5.5.5 Seal the desiccator jar (5.3.1) with its cover and place it in the oven (5.3.7) set at 50 °C. The fan shall be turned on for the first 30 min to distribute the peroxide vapour uniformly.

5.5.6 Remove the jar from the oven, quickly charge it with the addition of a second 0,12 ml of freshly prepared hydrogen peroxide solution (5.2.1) without allowing the desiccator jar to cool to room temperature. Replace it in the oven set at 50 °C. Turn on the fan for a second 30 min. The desiccator jar shall then be incubated with the fan turned off for 17 h at 50 °C, resulting in a total incubation of 18 h.

5.5.7 Remove the specimens from the desiccator jar

8) If the baffles are constructed so that they are spring loaded, the specimens can be attached by inserting the edges under the baffles.

and redevelop[9] them to reduce the silver which has been ionized during the test. Then wash and dry the specimens.

5.5.8 Examine the specimens visually under × 10 magnification for any evidence of red spots or redox blemishes. If there are no red spots, remeasure the specimens for status A blue density as specified in 5.5.1.

5.5.9 The change in density of the six uniform-density patches shall be corrected for the change in the D_{min} values by subtracting the change in D_{min} due to the treatment, as shown in annex A.

5.6 Significance

The extent to which the silver is attacked by hydrogen peroxide is evaluated by the magnitude of the change in blue density after the peroxide incubation. This is most easily shown by a plot of the change in blue density, corrected for the change in D_{min}, on the y-axis against the original blue density on the x-axis. The effectiveness of stabilizing treatments can be quantitatively measured by the deviation of this plot from the x-axis. A stabilizing solution which results in less than a 0,05 density change for all six uniform-density patches shall be considered to be an effective treatment against peroxides.

If the peroxide incubation results in the appearance of red spots on any of the specimens, a quantitative evaluation of the effect of the stabilizing treatment cannot be made. Therefore, such a treatment shall be considered to be not effective.

9) Redevelopment for 2 min at 25 °C in Kodak Prostar developer was found to be satisfactory for microfilms, and 30 s in Kodak Dektol developer for photographic paper prints. Developers should be at full strength. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

Annex A
(normative)

Correction of density values

A.1 General

The purpose of the dichromate bleach test and the hydrogen peroxide incubation test is to determine density changes in a silver image. However, changes in the D_{min} areas caused by gelatin stain or base discoloration are outside the interest of these tests. Consequently, changes in density of the silver patches shall be corrected for changes in the D_{min} area. This is illustrated by the examples in tables A.1 and A.2 for each test.

A.2 Dichromate bleach test

In the dichromate bleach test example shown in table A.1, the density of the 1,02 density patch decreased to 0,81 as a result of bleaching. However, there was a stain increase from 0,05 to 0,11. The net result of bleaching is different for transmission and reflection materials. For transmission, the density of the patch due to the silver is obtained by simple subtraction of the D_{min} values. For reflection, the density of the patch due to the silver is identical to that for transmission density, except that it includes a back correction equal to one-half of the increase in the D_{min} values. The following formula is used:

$$D_{patch}\ (corr) = D_{patch}\ (after\ bleach) - D_{min}\ (after\ bleach) + 0,5\ [D_{min}\ (after\ bleach) - D_{min}\ (original)]$$
$$= 0,81 - 0,11 + 0,5(0,11 - 0,05)$$
$$= 0,73$$

Table A.1 — Dichromate bleach test

	D_{min}	D_{patch}	D_{patch} (corr)	
			Transmission	Reflection
Original	0,05	1,02	0,97	0,97
After bleaching	0,11	0,81	0,70	0,73
% Density retention	—	—	72	75