42

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STANDARD

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Photography — Processed silver-gelatin type black-and-white film — Specifications for stability

Photographie — Film de type gélatino-argentique noir et blanc traité — Spécifications pour la stabilité

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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 10602 was prepared by Technical Committee ISO/TC 42, *Photography*.

This first edition cancels and replaces both ISO 4331:1986, which covered archival film on cellulose ester base, and ISO 4332:1986, which covered archival film on poly(ethylene terephthalate) base. It constitutes a consolidation and technical revision of these and, in addition, the scope has been extended to include archival use of radiographic film and microfilm and "medium-term" and "long-term" uses of all these films.

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

Introduction

Since 1930, great advances have been made in the use of photographic films for the preservation of records. The preservation of film records by governments, banks, insurance companies, industry and other enterprises has been stimulated by a recognition of the economies in storage space, organization, accessibility, and ease of reproduction that results from the use of film records.

During the early development period of the art of copying documents, 35 mm nitrate motion-picture film was sometimes used. This material is highly flammable and deteriorates rapidly under unfavourable storage conditions. Nitrate film is not suitable for film record use. The manufacture of nitrate film declined after World War II and was discontinued in most countries in the 1950's.

For many years the only safety films in commercial use were made on some type of cellulose ester base such as cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate. The useful life of safety cellulose-ester-type films is somewhat conjectural, since actual experience with commercial material extends back only to about 1908. However, these materials show severe degradation when exposed to high temperatures and particularly to high humidities [1] [4]. Laboratory incubation studies predict a useful life of several centuries [1] when stored under recommended conditions.

A second type of polymer safety film base belonging to the polyester class, known chemically as poly(ethylene terephthalate), was introduced commercially in 1956. This material has a number of advantages over the cellulose ester base such as greater strength, stiffness, tear resistance, flexibility, dimensional stability, and other characteristics, which make it superior for many photographic applications [2] [3]. Actual experience with polyester film is considerably shorter than with cellulose ester film although this material has been used for over 35 years. However, core set can create problems for some film types and adhesion was not completely satisfactory on some of the early polyester products (see annex E). Practical experience gained to date and accelerated ageing tests indicate that this film support is more stable than safety cellulose ester film base [1] [4].

More recent studies on the stability of silver-gelatin type films investigated the effect of residual hypo on the image permanence of radiographic films [5] and microfilms [6]. This work suggested modifications to the residual hypo limits and a more quantitative image stability test than given in ISO 4331:1986 and ISO 4332:1986. These changes are included in this International Standard. Additional studies are underway on other film types and future editions of this International Standard will include these when stability data become available. Currently, radiographic films, microfilms and "other" films are described. The scope of the "other" category should narrow as additional categories are specifically defined. Three levels of stability are specified — medium-term, long-term and archival, following the definitions given in ISO 5466.

This International Standard is intended to eliminate possible hazards to permanence attributable to the chemical or physical characteristics of the processed film. Some of these characteristics are the responsibility of the film manufacturer, some of the film processor and some are influenced by both. However, specifying the chemical and physical characteristics of the material does not, by itself, ensure satisfactory archival behaviour. It is essential to provide proper storage temperature and humidity and protection from the hazards of fire, water, fungus and certain atmospheric pollutants. Storage conditions for archival films are specified in ISO 5466.

Photography — Processed silver-gelatin type black-and-white film — Specifications for stability

1 Scope

1.1 This International Standard establishes the specifications for photographic films intended for medium-term, long-term and archival records; specifically, safety cellulose ester-base and polyester-base [poly(ethylene terephthalate)] films having silver-gelatin emulsions processed to produce a black-and-white silver image by negative, or full reversal processing.

1.2 This International Standard does not apply to films with colour images of any type, to silver images that have been altered by treatments such as toning, intensification or reduction, nor to films with a magnetic recording track. It does not apply to films with silver images produced by dry or thermal processing or by diffusion reversal or partial (halide) reversal processing. It does not apply to films that have been processed by a monobath or by those reversal processes that combine a developer and fix into one solution. It is not applicable to films where the silver salts are removed by other than thiosulfate solutions [7].

1.3 This International Standard does not apply to films to which lacquers have been applied.

1.4 This International Standard applies to films having ultrasonic or dielectric (induction heated) splices. It does not cover films with splices made by means of adhesive tape or solvent type splices[1].

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 5-3:1984, *Photography — Density measurements — Part 3: Spectral conditions.*

ISO 417:—[2], *Photography — Determination of residual thiosulfate and other related chemicals in processed photographic materials — Methods using iodine-amylose, methylene blue and silver sulfide.*

ISO 543:1990, *Photography — Photographic films — Specifications for safety film.*

ISO 1184:1983, *Plastics — Determination of tensile properties of films.*

ISO 5466:1992, *Photography — Processed safety photographic films — Storage practices.*

3 Definitions

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

3.1 archival storage conditions: Conditions suitable for the preservation of photographic film having permanent historical value.

NOTES

1 Archival storage conditions will prolong the useful life of both archival and non-archival films.

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[1] Solvent type splices are not recommended since they can retain traces of residual solvents containing peroxide which can pose some risk of oxidative attack on the silver image.

[2] To be published. (Revision of ISO 417:1977)

2 The term "archival" as used in photography and defined as in this International Standard is frequently being misapplied in related fields of imaging. ISO/TC 42 will therefore replace the term "archival storage" with "extended-term storage" or specify a "life expectancy (LE)" classification in future editions of its standards.

3.2 archival film: Photographic film suitable for the preservation of records having permanent value when stored under archival storage conditions, providing the original images are of suitable quality.

3.3 long-term film: Photographic film suitable for the preservation of records for a minimum of 100 years when stored under archival storage conditions, providing the original images are of suitable quality.

3.4 medium-term storage conditions: Conditions suitable for ensuring a minimum useful life of 10 years for photographic films.

3.5 medium-term film: Photographic film suitable for the preservation of records for a minimum of 10 years when stored under medium-term storage conditions, providing the original images are of suitable quality.

3.6 non-curl backing layer: Layer usually made of gelatin, applied to the side of the film base opposite that of the emulsion layer, for the purpose of preventing curl. It is comparable to the emulsion layer in thickness and is not removed in processing. (Antihalation or other layers removed in processing are excluded from this definition.)

3.7 safety photographic film: Film that meets the specifications with respect to ignition and burning time as defined in ISO 543.

3.8 safety cellulose-ester base: Film base composed mainly of cellulose esters of acetic, propionic, or butyric acids, or mixtures thereof.

3.9 safety poly(ethylene terephthalate) base: Polyester film base composed mainly of a polymer of ethylene glycol and terephthalic acid.

3.10 full reversal processing: Processing that includes a final fix and wash after the second development step.

4 Requirements for the film base

The base used for medium-term, long-term and archival record films shall be of a safety poly(ethylene terephthalate) or cellulose ester type and can be identified by the method described in 8.1.

5 Requirements for the processed film

5.1 Safety film

The film shall meet the requirements specified in ISO 543.

5.2 Amount of free acid

Different specifications and test methods for determining the amount of free acid are given for polyester base and cellulose ester base films. The polyester base shall not have an amount of free acid greater than the equivalent of 1 ml of 0,1 mol/l sodium hydroxide solution per gram of film and the cellulose ester base shall not have an amount of free acid greater than the equivalent of 0,5 ml of 0,1 mol/l sodium hydroxide solution per gram of film. The amount of free acid shall be measured in accordance with 8.3.

The volume of 0,1 mol/l sodium hydroxide equivalent to the amount of free acid of the processed film shall not increase by more than 0,5 ml over its original value after the accelerated ageing described in 8.2.

5.3 Tensile properties and tensile properties loss

The film samples shall be processed and dried under the conditions used for the film records. Processed films shall be tested for tensile properties as described in 8.4 and shall have a tensile strength and elongation at break as specified in table 1 for unheated film. The loss in tensile properties after accelerated ageing as described in 8.2 shall not exceed the percentage specified in table 1 for heated film.

Table 1 — Limits for tensile properties and tensile properties loss on ageing

	Base material	Tensile strength at break	Elongation at break %
Minimum permissible tensile properties of unheated film	Cellulose ester	80 MPa 1)	15
	Polyester	140 MPa	75
Maximum permissible loss in tensile properties of heated film compared with unheated film	Cellulose ester	15 %	30
	Polyester	15 %	30

1) 1 MPa = 10^6 N/m^2

6 Requirements for the emulsion and backing layers of processed film

6.1 Layer adhesion

6.1.1 Tape-stripping adhesion

The processed film shall not show any removal of the emulsion layer or backing layer when tested as described in 8.5.

6.1.2 Humidity-cycling adhesion

The emulsion layer or backing layer of the processed film shall not show separation or cracking that would possibly impair its intended use, when tested as described in 8.6 (see annex E).

6.2 Emulsion flow

The processed film shall not show any visual evidence of emulsion flow (caused by partial emulsion remelting) as a result of accelerated ageing of the processed film. Emulsion flow shall be determined as described in 8.7 when the accelerated ageing is performed as described in 8.2.

6.3 Blocking

Processed film shall show no evidence of blocking (sticking), delamination or surface damage when tested as described in 8.8. A slight sticking of the film samples that does not result in physical damage or a change in the gloss of the surface is acceptable.

6.4 Thiosulfate concentration

Films shall be fixed in solutions containing either sodium thiosulfate (hypo) or ammonium thiosulfate [7]. Hypo-eliminating agents containing oxidizing agents such as peroxides or hypochlorites shall not be used.3) After processing, the film shall not contain a greater concentration of residual thiosulfate calculated as thiosulfate ion $S_2O_3^{2-}$ than that specified in table 2 when determined by the test methods described in ISO 417.4)

The analysis for thiosulfate shall be made on a film sample from a clear area and shall be made within 2 weeks of processing (see annex B).

The test method does not measure any change in the sample between the time of processing and the time of analysis but is used to judge the keeping of the film following the time of the test.

Table 2 — Limits for thiosulfate concentration

Film type	Film classification	Maximum permissible concentration of thiosulfate1) g/m^2
Radiographic	Medium-term	0,100
	Long-term	0,050
	Archival	0,020
Microfilms	Long-term	0,030
	Archival	0,014
Other: fine grain	Archival	0,0072)
Other: coarse grain	Archival	0,020

1) For radiographic and "other" films having photographic layers on both sides, or a non-curl backing layer, values are for each side of the film. For microfilms, values are for the complete film.

2) The limit for fine grain archival films is currently less than for archival microfilms. This apparent anomaly is based on the results of a study of residual hypo that is currently underway. The work on microfilm has been completed but studies of other film types are not.

6.5 Residual silver compounds

The processed film shall not show more than a barely perceptible tint when tested in accordance with 8.9 (see annex C).

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3) Hypo-eliminating agents contain chemicals, usually strong oxidizing agents, which decompose thiosulfate (see annexes B and D). These are to be distinguished from hypo clearing baths, which are high ionic strength salt solutions. These facilitate the washing of thiosulfate from the film, but do not chemically alter the thiosulfate.

4) Three methods for measuring residual chemicals in film are described in ISO 417. All three methods are considered sufficiently reliable to report thiosulfate concentrations at the level of 0,014 g/m^2. The methylene blue method is considered reliable for thiosulfate concentrations of 0,007 g/m^2. The methylene blue and iodine amylose methods measure thiosulfate ion only and must only be run within two weeks of processing. The silver sulfide densitometric test method measures polythionate decomposition products and other residual chemicals in addition to thiosulfate. The method may be run more than two weeks after processing. To determine thiosulfate levels accurately with this method, a calibration curve for the particular film is necessary.

7 Image stability

The specifications and test methods for image stability are different for the different product types. ISO visual diffuse density or Status A blue-density shall be measured on a densitometer which has spectral conformance to ISO 5-3 and geometric conformance to ISO 5-2. Processed film samples shall be incubated as described in 8.10.

7.1 Radiographic films

An area of unexposed processed film shall be tested. The Status A blue-density change of the unexposed area shall be no greater than 0,05 density units after incubation for medium-term, long-term and archival films.

7.2 Microfilms

Two areas on the processed film sample shall be tested; one area of minimum density, the other having a visual diffuse density of 1,2 ± 0,1. The following criteria shall apply to the different film categories.

7.2.1 Long-term film

The minimum density area shall have a visual diffuse density of less than 0,4 after incubation. The difference in visual density between the two test areas shall be at least 0,8 after incubation.

7.2.2 Archival film

Neither the minimum nor the high density area shall change by more than 0,1 visual diffuse density units after incubation.

7.3 Other films

Samples of processed film containing representative image areas shall be tested. The film image shall show no degradation after incubation that would impair the film for its intended use.[5]

8 Test methods

8.1 Identification of film base

All emulsion and backing layers shall be removed from a sample of the unknown film, either by scraping or by the use of enzyme solution. All sublayers shall then be removed by scraping. A sample of the base material shall then be prepared by scuffing the surface with a suitable tool.

The general procedure is to move the scuffing device back and forth over the sample manually while exerting a very slight pressure. This removes the top layer of the base as a very fine dust, which is carefully brushed into a mortar. The sample shall be mixed with about 100 times its mass of potassium bromide previously ground to about 75 µm. A strip or pellet shall be prepared as described in [8]. An infrared absorption curve shall be obtained from the prepared pellet by means of an infrared absorption spectrophotometer. By comparing the infrared absorption curve for the unknown with curves for known polymers, the identity of the unknown can be established [9].[6]

8.2 Accelerated ageing conditions

Processed film shall be subjected to the accelerated ageing conditions to meet the requirements for increase in the amount of free acid, tensile properties loss and emulsion flow.

The test specimens shall be conditioned to (23 ± 1) °C and (50 ± 2) % relative humidity for at least 15 h. After conditioning, the specimens shall be placed in a moisture-proof envelope and the envelope shall be heat-sealed.[7] To prevent sticking between adjacent specimens, it may be necessary to interleave them with aluminium foil. A high ratio of film to air volume shall be ensured by squeezing out excess air prior to heat sealing. A separate envelope shall be used for each film sample. The envelopes shall be heated in an oven for 72 h at (100 ± 2) °C.[8]

An alternative method of incubating the specimens in a closed environment is by placing them in 25 mm borosilicate glass tubes [10]. Each tube shall have two flanged sections separated by a gasket to provide a moisture seal[9] and shall be held together by a metal clamp. Sufficient film specimens shall be used to provide a high ratio of film to air volume.

In subsequent subclauses, samples subjected to these accelerated ageing conditions are designated "heated". Comparison samples kept at standard conditions are designated "unheated".

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[5] Work is currently underway to establish more quantitative tests for other film types.

[6] It is difficult, although not impossible, to distinguish among cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate base by this method, but such separation is not necessary for the purpose of this International Standard.

[7] A suitable moisture-proof envelope is a metal foil bag that is coated on the inside with polyethylene for heat-sealing.

[8] Incubation is accomplished in a closed environment to prevent escape of any acid that is produced during incubation. Such acid can catalyse further base degradation.

[9] A suitable inert gasket can be made from poly(tetrafluoroethylene).

8.3 Determination of the amount of free acid

8.3.1 Specimen preparation

Measurements shall be made on two unheated and two heated specimens of imaged film of mass approximately 1 g to 2 g each. Weigh the specimens to the nearest 0,01 g. The films shall be heated in accordance with 8.2. All coatings shall be removed from the film base by scraping. Each specimen shall be cut into small pieces and accurately weighed prior to dissolving in the appropriate solvents.

8.3.2 Solution preparations

The polyester base and the cellulose ester base require different solvents.

Polyester samples shall be immersed in 30 ml of a purified 70/30 (*m*/*m*) mixture of *o*-cresol/chloroform.

WARNING — Chloroform is harmful if inhaled. Avoid breathing vapour, mist or gas. Use with adequate ventilation. If inhaled, move to fresh air. Contact should be avoided between chloroform and eyes, skin or clothing. Obtain medical attention immediately.

***o*-Cresol is toxic if swallowed. Contact should be avoided between *o*-cresol and eyes, skin or clothing. Wash after handling. In case of contact, flush eyes and skin thoroughly with water. Obtain medical attention immediately.**

The polyester support shall be dissolved by heating at 90 °C to 95 °C for 30 min or until the sample has dissolved.[10] The dissolved samples shall be cooled to room temperature.

Cellulose ester samples shall be immersed in approximately 80 ml of methylene chloride to which 40 ml of denatured ethyl alcohol is then added slowly.

WARNING — Methylene chloride is harmful if inhaled. Avoid breathing vapour, mist or gas. Use with adequate ventilation. If inhaled, move to fresh air. Contact should be avoided between methylene chloride and eyes, skin or clothing. Obtain medical attention immediately.

8.3.3 Titration

The polyester solution shall be titrated potentiometrically with standardized 0,1 mol/l tetrabutylammonium hydroxide using an automatic recording titrimeter.[11] The electrode of the titrimeter shall have been preconditioned for 24 h in the *o*-cresol/chloroform solvent mixture to prevent excessive instrumentation noise. A 30 ml blank, which has been heated for the same length of time as the samples, shall be titrated. Details of preparation of the standardized tetrabutylammonium hydroxide are given in annex A.

The cellulose ester solution shall be titrated with 0,1 ml/l sodium hydroxide, using cresol purple as the indicator. A blank titration shall also be made on the solvent mixture.

8.3.4 Calculation

The amount of free acid, A, expressed in equivalent millilitres of 0,1 mol/l sodium hydroxide per gram of film base, is calculated as follows for each sample:

$$A = \frac{(V_S - V_B)c_T}{0{,}1m}$$

where

V_S is the volume of titrant used for the sample, in millilitres;

V_B is the volume of titrant used for the blank, in millilitres;

c_T is the concentration of the titrant, in moles per litre;

m is the mass of the sample, in grams.

The titration shall be carried out in duplicate on separately prepared solutions. The average amount of free acid for the unheated and heated film samples shall be calculated and reported separately.

8.4 Tensile property test for processed films

8.4.1 Specimen preparation

Processed film already in 16 mm format may be tested in this width. In the case of perforated 16 mm film, specimens shall be cut from between the perforations. Film in other sizes shall be cut into sections 15 mm to 16 mm wide and at least 150 mm long using a sharp tool that does not nick the edges of the sample. Five specimens are required for the unheated film and five specimens for the heated film. The specimens to be heated and the control specimens shall be cut alternately and contiguously from a single piece of film. The thickness of each specimen shall be measured with a suitable gauge to the nearest 0,002 mm and the width to the nearest 0,1 mm.

8.4.2 Accelerated ageing

Five specimens shall be subjected to accelerated ageing as described in 8.2.

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[10] Precautions should be taken to prevent excessive evaporation of the solvent.

[11] During titration, the burette tip should be immersed into the solution as far as possible and also as far from the electrodes as practical. The stirring rate should be as rapid as can be maintained without causing bubbles.

8.4.3 Conditioning

All specimens, both unheated and heated, shall be conditioned at (23 ± 1) °C and (50 ± 2) % relative humidity for at least 15 h. This may be accomplished by means of an air-conditioned room or a conditioning-air cabinet. The specimens shall be supported in such a way as to permit free circulation of air around the film and the linear air velocity shall be at least 150 mm/s.

8.4.4 Procedure

The film specimens shall not be removed from the conditioning atmosphere for testing. The tensile strength and percentage elongation at break of unheated and heated film specimens shall be tested alternately by means of a tensile testing machine, as specified in ISO 1184.

The initial grip separation shall be 100 mm and the rate of grip separation shall be 50 mm/min. The tensile strength and elongation at break shall be calculated separately for the unheated and heated film.

8.5 Tape-stripping adhesion test

8.5.1 Specimen preparation

Although the dimensions of the processed film specimen are not critical, one dimension shall be at least 150 mm. Four specimens shall be used for the emulsion surface and four specimens for the backing layer, if present.

8.5.2 Conditioning

Specimens shall be conditioned as described in 8.4.3.

8.5.3 Procedure

The film specimens shall not be removed from the conditioning atmosphere for testing. A strip of pressure-sensitive plastic-base adhesive tape about 150 mm long shall be applied to the surface of the processed film. The tape shall be pressed down with thumb pressure to ensure adequate contact, leaving enough tape at one end to grasp. No portion of the tape shall extend to the edges of the film specimens or extend to film perforations. The specimen shall be held firmly on a flat surface and the tape rapidly removed from the film surface. This shall be accomplished by peeling the tape back on itself and pulling the end so that it is removed from the film at an angle of approximately 180°. Removal by the tape of any portion of the surface layer on any of the specimen shall be considered failure.

The results of the tape-stripping test can be very dependent upon the adhesive tape used if the bonding force between it and the particular film surface under test is not sufficiently high. For this reason, a minimum bonding force is specified for this test. This bonding force shall be determined by applying the adhesive tape to the film surface in the same manner as described in the tape-stripping test. The tape shall be rapidly peeled back from the film surface at an angle of approximately 180°. The peelback force required to separate the tape from the film shall be measured by a suitable device such as a strain gauge or spring scale capable of reading the maximum force used. A bonding force of at least 90 N per millimetre of tape width is required.

8.6 Humidity-cycling adhesion test

8.6.1 Specimen preparation

Two specimens of processed film shall be selected from an area of high silver density. The specimens should be either 50 mm × 50 mm, or 50 mm long × the film width where the size of the film permits, but the dimensions are not critical provided all specimens are of uniform size.

8.6.2 Procedure

The test specimens shall be mounted in a specimen rack and placed in a glass laboratory desiccator jar in such a way that they are freely exposed to the required conditioning atmospheres. The jar shall be put into a forced-air-circulating oven for 8 h at (50 ± 2) °C. The atmosphere within the jar shall be maintained at 96 % relative humidity, which can be obtained by keeping a saturated solution of potassium sulfate in water [11] in the bottom of the jar.[12] It shall be ensured that the saturated solution contains an excess of undissolved crystals at 100 °C. The undissolved crystals shall be completely covered by a layer of saturated salt solution and the surface area of the solution should be as large as practical. The jar and salt solution shall be kept at 100 °C for at least 20 h prior to use to ensure adequate equilibrium.

After 8 h, the specimens and specimen rack shall be placed for a further 16 h in a second desiccator jar that is also in the same oven. The atmosphere within the second jar shall be maintained at 11 % relative humidity, which can be obtained by keeping a saturated solution of lithium chloride in water [11] in the bottom of the jar.[12]

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[12] The relative humidity is based on the normal vapour pressure of the salt solution but the relative humidity tolerances cannot be specified.

A period of 8 h at the high humidity and 16 h at the low humidity shall constitute one cycle.[13] The film specimen shall be subjected to twelve humidity cycles, after which the film specimens shall be removed from the specimen rack and the emulsion and any backing layer examined for any evidence of peeling, flaking or cracking produced as a result of the humidity-cycling treatment.[14] The film shall be examined under the magnification and lighting conditions that are normal for the end use of the product. During a weekend interruption in the cycling procedure, the film specimens shall be kept at (50 ± 2) °C and 11 % relative humidity.

8.7 Emulsion flow test

Measurements shall be made on two heated specimens of processed film. Each specimen shall contain a photographic image of a grid pattern or of printed material. Film specimens shall be subjected to accelerated ageing as described in 8.2. After incubation, the photographic images on the heated samples shall be visually examined for any image change caused by flow of the emulsion. This visual examination may be facilitated by comparison with the images on unheated specimens.

8.8 Blocking test

At least five specimens of processed film shall be conditioned to 62 % relative humidity at (40 ± 2) °C. The specimens should be 50 mm × 50 mm where the size of the film permits, but the dimensions are not critical provided all specimens are of uniform size. The specimens shall be placed in a glass laboratory desiccator jar so that they are freely exposed to the required conditioning atmosphere for at least 15 h. The jar containing the specimens shall be put into a forced-air-circulating oven at (40 ± 2) °C. A relative humidity of approximately 62 % can be obtained by keeping a saturated solution of sodium nitrite [12] in water at the bottom of the jar.[12] It shall be ensured that the saturated solution contains an excess of undissolved crystals at 100 °C. The undissolved crystals shall be completely covered by a layer of saturated salt solution and the surface area of the solution should be as large as practical. The jar and salt solution shall be kept at 100 °C for at least 20 h prior to use to ensure adequate equilibrium. After moisture equilibrium is attained, the jar shall be removed from the oven. Without removing the film specimens from the jar, at least five film specimens shall be stacked so that the emulsion surface of one specimen is against the back surface of the adjacent specimen. The stack shall be placed under a uniform pressure of 35 kPa. This can be accomplished by placing a weight on the film stack, the dimensions of the weight being greater than those of the film specimens. The jar containing the weighted stack shall be put back into the forced-air-circulating oven for 3 days at 40 °C.

Alternatively, the temperature and humidity conditions may be achieved by means of conditioning-air cabinets or air-conditioned rooms.

The film stack shall be removed from the oven and allowed to cool. The film specimens shall then be individually removed from the stack and observed for evidence of film blocking (sticking) (see 6.3).

8.9 Residual silver compound test

Two specimens of processed film of any available size shall be tested on both sides. These specimens shall be taken from the end of the processing run. The film shall be blotted dry if necessary, and a clean area shall be spotted with a freshly prepared 0,2 % aqueous solution of sodium sulfide. The reagent shall be washed away or blotted up after 3 min.

If there is more than a barely perceptible tint, a reference specimen shall be prepared. The reference specimen shall be:

- of the same film type and preferably taken from the same lot;
- fixed successively for 5 min in each of two duplicate fresh fixing bath containing 240 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) per litre; and
- washed for 30 min in running water that is flowing at a rate that will fill the vessel once every 5 min.

The film shall be air dried and tested with the sodium sulfide solution as mentioned in the previous paragraph.

Any stain in the test specimen greater than that of the reference specimen is an indication of residual silver salts.

8.10 Image stability test

8.10.1 Sample preparation

Specimens of film shall be exposed to the specified densities or image as indicated in table 3. These differ for the different film types. An appropriate specimen

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[13] This can be most easily accomplished by placing the specimens in the 96 % relative humidity jar in the morning and in the 11 % relative humidity jar in the evening.

[14] Films can sometimes exhibit what appear to be small pinholes in the image after processing. These can be caused by dirt or dust particles on the emulsion surface at the time the raw film is exposed and should not be confused with holes or cracks in the emulsion layer. The existence of such pinholes in the image prior to humidity cycling should be noted so that their presence does not lead to its false interpretation as an adhesion weakness.

size is 50 mm × 50 mm for sheet film products, or 50 mm long × the film width for roll film products.

8.10.2 Specimen incubation

Two specimens shall be mounted in a conditioning-air oven so that they are freely exposed to the surrounding air. Temperature shall be controlled to within 2 °C and relative humidity to within 2 % of the values given in table 3.

An alternative incubation method is as follows. The film shall be conditioned to the specified relative humidity for at least 8 h at ambient temperature. This may be accomplished by means of an air-conditioning room or a conditioning-air cabinet. The specimens shall be supported in the conditioning-air cabinet in such a way as to permit free circulation of air around the film, and the linear air velocity shall be at least 150 mm/s. The film shall then be heat sealed in a moisture-proof metallic-foil envelope after the air has been squeezed out.

8.10.3 Incubation conditions

Film specimens shall be incubated under the conditions specified in table 3. A description of how these conditions were chosen appears in annexes F and G.

8.10.4 Measurement

Radiographic film shall be measured for Status A blue-density and microfilms shall be measured for visual diffuse density, both before and after incubation.

Densities shall be measured on a densitometer having a spectral conformance to ISO 5-3 and geometric conformance to ISO 5-2. The samples shall meet the density criteria given in 7.1 and 7.2.

Other film types shall be compared visually with an unincubated comparison sample. The film shall meet the criterion given in 7.3.[15]

Table 3 — Conditions for image stability test

Film type	Sample density or image	Film classification	Duration days	Incubation conditions Temperature °C	Incubation conditions Humidity % RH
Radiographic films	Unexposed area	Medium-term	14	68	60
		Long-term	14	77	60
		Archival	14	85	60
Microfilms	Areas of minimum density and $D = 1{,}2 \pm 0{,}1$	Long-term	14	60	60
		Archival	30	60	60
Other: fine grain	Representative image	Archival	30	60	70
Other: coarse grain	Representative image	Archival	30	60	70

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[15] Work is currently underway to establish more quantitative tests for other film types.

Annex A
(normative)

Preparation of standard tetrabutylammonium hydroxide

Polyester bases inherently have carboxyl groups incorporated in their molecular structure. In chemical terminology, these are referred to as free acids and the amount present is expressed as the volume of a standard sodium hydroxide solution required to neutralize 1 g of polyester base. The intent of the test specified in 5.2 is to ensure that the base is chemically stable and also that it will not be adversely affected by the image-bearing or other layers. Thus, the entire film is heated in accordance with 8.2 to simulate long-term ageing. However, all the layers are removed from the base prior to determining the amount of free acid to simplify the analytical procedure.

A primary 0,1 mol/l benzoic acid standard solution is used to standardize a tetrabutylammonium hydroxide (TBAH) titrant, which in turn is titrated against the polyester base to determine the amount of free acid. The nominal 0,1 mol/l benzoic acid primary standard is prepared by weighing (1,22 ± 0,01) g of benzoic acid into a 100 ml volumetric flask and subsequently adding a purified 70/30 (*m*/*m*) mixture of *o*-cresol/chloroform.

WARNING — Chloroform is harmful if inhaled. Avoid breathing vapour, mist or gas. Use with adequate ventilation. If inhaled, move to fresh air. Contact should be avoided between chloroform and eyes, skin or clothing. Obtain medical attention immediately.

***o*-Cresol is toxic if swallowed. Contact should be avoided between *o*-cresol and eyes, skin or clothing. Wash after handling. In case of contact, flush eyes and skin thoroughly with water. Obtain medical attention immediately.**

The concentration of the primary benzoic acid standard, c_P, in moles per litre, is calculated from:

$$c_P = \frac{0{,}1 m_B}{1{,}22}$$

where m_B is the mass of benzoic acid used, in grams.

The primary standard is then used to determine the molarity of the TBAH base titrant.

A 25 % (*m*/*m*) solution of TBAH is prepared by dissolving 25 g in 75 g of water. The nominal 0,1 mol/l TBAH titrant solution is prepared by adding 90 ml isopropanol to 10 ml of the 25 % (*m*/*m*) aqueous TBAH solution. This is standardized against the primary benzoic acid solution by pipetting exactly 1 ml of benzoic acid into a 50 ml beaker and adding 30 ml of a 70/30 (*m*/*m*) mixture of *o*-cresol/chloroform. This solution is titrated with TBAH base titrant using an automatic recording titrimeter in the prescribed manner. A similar titration is made with a blank 30 ml sample of the *o*-cresol/chloroform mixture. Both titrations are made in duplicate. The concentration of the TBAH base titrant c_T, in moles per litre, is calculated from:

$$c_T = \frac{V_P c_P}{V_S - V_B}$$

where

V_P is the volume of the primary benzoic acid standard, in millilitres;

c_P is the concentration of the primary benzoic acid standard, in moles per litre;

V_S is the volume of TBAH titrant used for the sample, in millilitres;

V_B is the volume of TBAH titrant used for the blank, in millilitres.

EXAMPLE

If 1,00 ml of 0,102 mol/l primary standard is titrated with 1,147 ml of TBAH titrant and 30 ml of blank is titrated with 0,032 ml of TBAH titrant, then:

$$c_T = \frac{1{,}00 \times 0{,}102}{1{,}147 - 0{,}032} = 0{,}091 \text{ mol/l}$$

Annex B
(informative)

Washing and the effect of residual thiosulfate on the developed silver image

The preservation of silver-gelatin type photographic film is dependent on the products which are still present after washing. The maximum content of residual thiosulfate[16] and residual silver compounds is specified in 6.4 and 6.5. Water used for washing should be colourless and free from substances in suspension. Drinking water is generally pure enough for washing purposes.

A washing water temperature maintained at a level between 15 °C and 25 °C is generally suitable and strikes a balance between the danger of swelling introduced by higher temperatures and the decrease in the rate of solubility of the salts being removed at lower temperatures. Some films can tolerate higher temperatures. Washing in well-agitated running water for 15 min at a temperature of 20 °C is generally satisfactory, provided that the films are not in contact with one another and that water is renewed at their surfaces. For most automatic machines (droplet, jets, etc.), the washing time is shorter and the water temperature is higher. The wash water temperature should be within 3 °C of the developer temperature.

Ion-exchange washing accelerators may be used. For instance, films may be soaked in a bath containing 20 g of anhydrous sodium sulfite per litre before washing.

Excessive thiosulfate ion retained by the film produces one or more of the following phenomena:

a) yellow-brown discolouration in the low-density areas of the film;

b) bleaching or loss of density in the image areas; or

c) an increase in density of the image areas [5] [6].

The test for residual thiosulfate ion is made on non-image or clear areas of the film because this is where the thiosulfate ion concentration, as measured by the methylene blue method, will not change appreciably over a period of 2 weeks.

Tests have shown that even at fairly high residual thiosulfate ion levels, adverse changes are quite gradual for 60 % relative humidity incubations. The limits of residual thiosulfate ion permitted in this International Standard are based on the incubations described in annexes F and G and are sufficiently low to minimize changes under recommended storage conditions.

The amount of thiosulfate ion retained in a processed film is dependent to a considerable degree on the composition of the fixing bath [13] [14]. Acid hardening fixing baths (which contain aluminium salts) condition the gelatin in the emulsion so that the thiosulfate ion is retained more tenaciously than in a non-hardening bath. However, a non-hardening fixing bath should be used with caution because the gelatin can become soft. Ammonia or hypo eliminators which contain oxidizing agents (such as hypochlorite and peroxides) should not be used.

The degree of change that can be tolerated in films depends upon their intended use. For textual records, legibility can be the sole consideration. For picture records, even a slight amount of discolouration or bleaching, particularly if non-uniform can be unacceptable. It is believed that the residual thiosulfate ion specified provides a sufficient margin of safety for medium-term, long-term and archival record film under storage conditions specified in ISO 5466.

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[16] The term thiosulfate is used generally to include its decomposition products, the polythionates and silver complexes.

Annex C
(informative)

Effect of residual silver compounds on the developed silver image

Residual silver compounds and complexes are an important cause of image layer degradation in aged processed photographic films. The silver of the complex ion can combine with sulfur produced by the decomposition of the thiosulfate or can react with atmospheric contaminants to produce discolouration. At the present state of knowledge it is not possible to specify a safe maximum for residual silver compounds in quantitative terms. However, it is believed that the quantity of residual silver compounds will be satisfactorily low when the film passes the test for residual silver compounds specified in 6.5.

To ensure that the fixing bath is suitable, it is recommended that the amount of silver be less than 0,5 % (*m*/*m*) in the case of a bath containing crystallized sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) or less than 0,8 % (*m*/*m*) in the case of a bath containing anhydrous ammonium thiosulfate [$(NH_4)_2S_2O_3$]. In order to minimize defects in microfilms known as "ageing blemish microspots", the iodide content (as KI) in the fixing bath for such products should be between 0,1 g/l and 0,5 g/l (see annex D).

A high concentration of silver complexes in the fixing bath, oxidants in the wash water and film-drying conditions that provide an unclean atmosphere or impart a case-hardening effect on the emulsion are considered undesirable factors in the preparation of film. However, they do not appear to preclude the preparation of film suitable for records when the product is stored as recommended.

Annex D
(informative)

Microscopic spots and blemishes

In 1961 it was discovered that some processed negative microfilms on cellulose ester base in storage for between 2 years and 20 years can develop microscopically small coloured spots or blemishes. The fogged leader at the outside of the roll is more frequently affected by the blemishes, which are generally red or yellow and smaller than the image characters (for example, a typewritten cipher reduced 20 times) on the microfilm. On occasion, these spots are observed further into the roll and appear in image areas. Evidence to date indicates that negative microfilms on polyester base are neither more nor less susceptible to microscopic blemishes than microfilms on cellulose ester base.

The spots are caused by the oxidation of the image silver and the migration of the silver ion to localized areas. The colour is due to colloidal silver [15] [16]. Oxidizing agents that can cause image degradation are aerial oxygen, whose action on the film is strongly accelerated by moisture, and atmospheric contaminants (such as ammonia, peroxides, ozone, sulfur dioxide, hydrogen sulfide and nitrogen oxides, all occuring in industrial atmospheres). Peroxides can be present in some varieties of wood and cardboard containers commonly used in storing film and can also be formed as the result of ageing of paper inserts, curing of paints etc.

The conditions under which microfilm is processed have been found to play a role in the development of the blemishes when the film has been improperly stored in a humid atmosphere. Good processing techniques are essential so that the film emerges from the process free of water and chemical spots, dirt, dust, scratches and other blemishes. Washing procedures should provide uniform removal of the thiosulfate and the associated silver compounds. Drying should be uniform and extremes of temperature should be avoided. A small quantity of potassium iodide in the fixing bath, combined with proper storage conditions, has been found to provide some protection against these blemishes in microfilm [17]. Small amounts of residual thiosulfate (at the limits of analytical detectability) can minimize blemishes caused by improper storage conditions (i.e. not in accordance with ISO 5466.)

It should be emphasized that the conditions under which microfilm is stored play a vital role in the development of these defects. Storage in cool, dry air that is free of oxidizing gases or vapours is important. Storage in acceptable metal or plastic cans rather than with paper or in cardboard cartons, which produce peroxides with age, is recommended.

Annex E
(informative)

Emulsion adhesion

The adhesion of the photographic and backing layers of some early films to the poly(ethylene terephthalate) base was not quite as good in all respects or under all conditions as the adhesion of the layers to the cellulose-ester-type bases. The extreme chemical inertness of the poly(ethylene terephthalate) base made the problem of adhesion much more difficult. In very low relative humidities, for example, the gelatin photographic and backing layers contract and the contraction imposes severe stresses on the adhesion of the gelatin layers to the base. Cycling relative humidities from moderate to very low causes alternate expansion and contraction of the gelatin layers, which can be particularly severe on the adhesive bond. The magnitude of this stress on the bond is very dependent on the thickness and physical characteristics of the gelatin layers, which differ with each type of film.

Under extreme conditions of elevated temperature and low or cycling relative humidities, gelatin photographic layers and backing layers on polyester base sometimes develop adhesion defects, such as slight edge peeling, flaking, emulsion cracking, etc., while similar layers on cellulose base under the same conditions do not exhibit these defects or do so to a lesser degree. For this reason, the relative humidity is extremely important for permanent record storage. The recommended environment conditions for archival storage of gelatin binder layers on polyester base are temperatures less than 21 °C and a relative humidity between 30 % and 50 %. It is therefore recommended that polyester base films for permanent records not only meet the requirements of this International Standard but also be stored under proper storage conditions. These are specified in ISO 5466.

Annex F
(informative)

Accelerated image stability test for radiographic films

The experimental method used to derive the residual thiosulfate levels and film lifetimes is based on the data that appear in [5]. Eight radiographic films were exposed and processed in suitable processors by adding various amounts of fixer to the wash tanks of the processors. This non-recommended processing cycle yielded processed film specimens with a wide range of residual thiosulfate levels. The methylene blue method described in ISO 417 was used to measure residual thiosulfate levels. The processed film specimens were incubated for a series of durations in dark chambers at 60 % relative humidity and temperatures from 93 °C to 52 °C. All specimens were free-hung in chambers where temperature and humidity were both controlled. Status A blue-density measurements were made before and after the keeping periods for all specimens.

Status A blue-density change in the minimum density area was shown to be the sensitometric parameter most sensitive to increasing residual thiosulfate levels. Practical radiographs that had been incubated were examined by people with experience in X-ray diagnosis. They concluded that a yellow-brown stain increase of 0,05 Status A blue-density units would be just noticeable to a diagnostician. For each film and for each temperature, the storage time to produce this sensitometric change was determined for each residual thiosulfate level.

The logarithm of the time for the stain build-up to occur for each incubation temperature is plotted against the reciprocal of the thermodynamic (absolute) temperature. Curves are plotted in figure F.1 for experiments which showed density change. Extrapolation down to room temperature of 23 °C indicated the time for the stain build-up to occur for room-temperature storage at 60 % relative humidity. The results of these extrapolations justify the limits specified in table 2. The limits are conservatively based on the extrapolations of the experimental data. The limits are also conservative because the experiment was done at 60 % relative humidity, which is higher than the maximum recommended storage relative humidity of 50 % for radiographic film. The incubation criteria for the accelerated tests in 8.10 were based on results of the eight radiographic films mentioned previously. The times were based on the least stable of these films and are conservative estimates.