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INTERNATIONAL STANDARD

ISO 10602

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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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Annexes

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.

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 thiosulfate[1] g/m²
Radiographic	Medium-term	0,100
	Long-term	0,050
	Archival	0,020
Microfilms	Long-term	0,030
	Archival	0,014
Other: fine grain	Archival	0,007[2]
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/m². The methylene blue method is considered reliable for thiosulfate concentrations of 0,007 g/m². 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".

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.

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.