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Imaging materials — Processed colour photographs — Methods for measuring thermal stability

Matériaux pour l'image — Photographies couleurs après traitement — Méthodes de mesure de la stabilité thermique

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee 42, *Photography*.

This second edition cancels and replaces the first edition (ISO 18936:2012), which has been technically revised.

The main changes compared to the previous edition are as follows:

- the test methods for environmental stress factors have been changed to align with ISO 18944;
- the calculations and computations section has been removed as they are now contained in ISO 18944;
- Annex A has been removed as the method for interpolation is now contained in ISO 18944:2018, Annex B;
- the usage and reporting requirements have been updated to ensure consistency within the documents of the ISO 189## family.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document covers the methods and procedures for measuring the long-term, dark storage stability (thermal stability) of colour photographs.

Today, the majority of photographs are made with colour dyes and pigments. The length of time that such photographs are to be kept can vary from a few days to many hundreds of years, and the importance of image stability can be correspondingly small or great. Often the ultimate use of a particular photograph may not be known at the outset. Knowledge of the useful life of colour photographs is important to many users, especially since stability requirements often vary depending upon the application. For museums, archives and others responsible for the care of colour photographic materials, an understanding of the behaviour of these materials under various storage and display conditions is essential if they are to be preserved in good condition for long periods of time.

Any change in density, contrast or stain, whether due to colourant fading, changes in colourant morphology or discolouration of residual substances will change the appearance of the photograph.

The most damaging change tends to be contrast balance distortions brought about by differential fading of the three image colourants. These manifest themselves as shifts in colour balance from highlights to shadows that are especially noticeable in a scale of neutrals, for example a shift from magenta to green due to fading of the photograph's magenta image colourant, or from yellow to blue or cyan to red due to fading of the yellow or cyan colourant.

The second most consequential change is that caused by an increase in stain. The result may simply be a discolouration of the D_{min} areas (unexposed processed media or unprinted substrate) or a change in the D_{min} colour balance.

Cyan, magenta, yellow, and sometimes black, red, green and blue colourants that are dispersed in transparent binder layers, or absorbed onto special receiver layers coated onto transparent or white opaque supports, form the images of most modern colour photographs. Colour photographic images typically fade during storage and display; they will usually also change in colour balance because the image colourants seldom fade at the same rate. In addition, a yellowish (or occasionally another colour) stain may form and physical degradation may occur, such as embrittlement and cracking of the support and image layers. The rate of fading and staining is governed principally by the intrinsic stability of the colour photographic material and by the conditions under which the photograph is stored and displayed. The quality of chemical processing or post-processing is another important factor. Post-processing treatments and, in the case of digitally generated photographs, post-production treatments, such as application of lacquers, plastic laminates and retouching colours, also may affect the stability of colour materials.

The three main factors that influence storage behaviour or dark stability are the temperature and relative humidity (RH) of the air that has access to the photograph, as well as atmospheric pollutants to which the photograph is exposed. High temperature, particularly in combination with high relative humidity, will accelerate the chemical reactions that can lead to degradation of one or more of the image colourants. Low-temperature, low-humidity storage, on the other hand, can greatly prolong the life of photographic colour images for typical materials. Other potential causes of image degradation are microorganisms and insects.

Most modern photographs degrade too slowly under normal room conditions to permit evaluation of their dark storage stability within reasonable periods. However, it is possible to assess the probable, long-term changes of some photographs under low and moderate storage conditions with accelerated, high-temperature tests, because recognizable losses in image quality under high temperatures are apt to be generated also under milder temperatures, if at a slower pace. The effects of relative humidity on thermal degradation can also be evaluated with Arrhenius tests conducted at two or more humidity levels.

Long-term changes in image density, colour balance and stain level can be reasonably estimated only when good correlation has been confirmed between accelerated tests and actual conditions of use.

Density changes induced by the test conditions and measured during and after incubations include those in the support and in the various auxiliary layers that may be in a particular product. With most materials, however, the major changes occur in the image-bearing layer. An exception to this is found in some inkjet papers where the inks are thermally stable and substrate yellowing is the failure mode (see Reference [9]).

The tests for predicting the stability of colour photographic images in dark storage are based on an adaptation of the Arrhenius method described by Bard et al. (see References [2] and [3]) and earlier references by Arrhenius, Steiger and others (see References [4], [5] and [6]). Although this method is derived from well understood and proven theoretical precepts of chemistry, the validity of its application to predicting changes of photographic images rests on empirical confirmation. Although many chromogenic-type colour products yield image fading and staining data in both accelerated and non-accelerated dark ageing tests that are in agreement with the Arrhenius relationship, some other types of products do not. For example, integral-type instant colour print materials often exhibit atypical staining at elevated temperatures. The treatment of some chromogenic materials at temperatures above 80 °C and 60 % RH may cause the loss of incorporated high-boiling solvents and abnormal image degradation. The dyes of silver dye-bleach images deaggregate at combinations of very high temperature and high relative humidity, causing abnormal changes in colour balance and saturation (see Reference [7]). In general, photographic materials tend to undergo dramatic changes above 60 % RH (especially at the high temperatures used in accelerated tests) owing to changes in the physical properties of gelatine and other binder materials. Lower maximum relative humidity may need to be tested for some of the more humidity-sensitive inkjet materials because of phase changes such as melting point or glass transition temperature.

Imaging materials — Processed colour photographs — Methods for measuring thermal stability

1 Scope

This document describes test methods for determining the long-term dark storage stability of colour photographic images.

It is applicable to colour photographic images made with traditional photographic materials. These images are generated with systems such as chromogenic, silver dye-bleach, dye transfer, dye-diffusion-transfer “instant”, and similar systems. The test method specified in this document also covers the dark-stability of digital colour images produced with dry- and liquid-toner electrophotography, thermal dye transfer (sometimes called “dye sublimation”), and inkjet printing systems.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

ISO 13655, *Graphic technology — Spectral measurement and colorimetric computation for graphic arts images*

ISO 18913, *Imaging materials — Permanence — Vocabulary*

ISO 18924, *Imaging materials — Test method for Arrhenius-type predictions*

ISO 18941, *Imaging materials — Colour reflection prints — Test method for ozone gas fading stability*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18913 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
operational fluctuations
positive and negative deviations from the setting of the sensor at the operational control set point during equilibrium conditions in a laboratory-accelerated weathering device

Note 1 to entry: The operational fluctuations are the result of unavoidable machine variables and do not include measurement uncertainty. The operational fluctuations apply only at the location of the control sensor and do not imply uniformity of conditions throughout the test chamber.

[SOURCE: ASTM G 113]

3.2
operational uniformity
range around the operational control point for measured parameters within the intended exposure area within the limits of intended operational range

[SOURCE: ASTM G 113]

3.3
uncertainty of measurement
parameter, associated with the result of a measurement, that characterizes the dispersion of the values which could be reasonably attributed to the measurement

Note 1 to entry: The parameter may be, for example, a standard deviation (or a given multiple of it), or the half-width of an interval having a stated confidence level.

Note 2 to entry: Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

Note 3 to entry: It is understood that the result of the measurement is the best estimate of the value of the measurement, and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

[SOURCE: ASTM G 113]

4 Requirements

This document specifies a set of recommended test methods with associated requirements for permitted reporting. Data from these tests shall not be used to make life expectancy claims, such as time-based print lifetime claims, either comparative or absolute. The conversion of data obtained from these methods for the purpose of making public statements regarding product life shall be in accordance with the applicable document(s) for specification of print life.

The test methods in this document may be useful as stand-alone test methods for comparison of the stability of image materials with respect to one specific failure mode. The data from the test methods of this document may be used in stand-alone reporting of the absolute or comparative stability of image materials with respect to the specific failure mode dealt with in this document, when reported in accordance with the reporting requirements of this document. Caution shall be used when comparing test results for different materials. Comparisons shall only be made when using equipment with matching specifications, under matching test conditions.

Further clarification is required for this method because it makes use of the Arrhenius methodology which may directly lead to a predicted product lifetime. Fundamentally, the Arrhenius method defines a rate of change (see ISO 18924). This document shall use the ISO 18924 Arrhenius method only as a predictor of rate of change for chemical reactions, not as a predictor of print longevity.

5 Sample preparation

5.1 Target selection

For general testing purposes, users of this document are free to choose whatever target, patches and starting densities they feel are appropriate for their testing needs. An example of such a target is included in ISO 18944[26], along with requirements and recommendations for sample preparation. Applicable documents(s) for specification of print life may require the use of specific targets. Other recommendations for sample preparation are contained in ISO 18909[20]. Image prints may also be used. When specific starting densities are desired or required, there may not be a step on a printed test target that corresponds to the exact desired density. Interpolation between two neighbouring density patches can be used to predict the values for the exact desired starting density. See ISO 18944:2018, Annex B for details on interpolation between two neighbouring density patches.

5.2 Use of replicates and reference samples

At least two replicate prints are required. Replicates shall be located for testing in different regions of the test chamber volume.

It is recommended that reference samples be included in every exposure test to track consistency of the test procedures as well as unintended changes of test conditions (see Reference [21]).

6 Holding and measurement conditions

Measurements and sample holding for measurement and next test phase preparation shall be conducted in a controlled environment with no time constraint, or in a less controlled environment with a time constraint. The measurement environment and sample holding environment can influence measured densities.

NOTE 1 "Sample holding environment" refers to the environment in which samples are held between test phases, such as before and after measurement, while the samples are not in the active test environment.

The controlled sample holding environment with no time constraint shall meet the following set of conditions: samples shall be kept in the dark at 23 °C ± 2 °C and at a relative humidity of (50 ± 10) % while waiting for measurement and while holding between test stages.

The sample holding environment shall be ozone-free (<2 nl/l average ozone concentration over any 24 h period) for ozone-sensitive samples.

NOTE 2 1 nl/l = 1 ppb (1 × 10^{-9}). Although the notation "ppb" (parts per billion) is widely used in the measurement and reporting of trace amounts of pollutants in the atmosphere, it is not used in this document because it is language-dependent.

Ozone sensitivity shall be determined in accordance with ISO 18941; ISO 18944 may also be used. A material that is not sensitive to ozone shall have demonstrated no measurable $D_{\min}$ (unexposed processed media or unprinted substrate) or printed patch colour change at ambient ozone exposure levels and measurement condition temperature and humidity, over time periods consistent with measurement and test staging time periods.

The controlled measurement environment with no measurement process time constraint shall meet the following set of conditions: ambient illuminance on the sample surface no greater than 200 lx, temperature of 23 °C ± 2 °C and a relative humidity of (50 ± 10) %, and ozone-free <2 nl/l average ozone concentration over any 24 h period) for ozone-sensitive samples.

When sample holding and/or measurement are conducted in a less controlled environment, samples shall be held or measured in the less controlled environment for a maximum of 2 h for each test stage. The less controlled environment may be unfiltered for ozone, and shall have a maximum relative humidity of 75 % and maximum temperature of 30 °C, with ambient illuminance on the sample surface less than or equal to 1 000 lx.

NOTE 3 Stray light decreases the accuracy of measurements taken in less controlled lighting environments. Shielding the measurement instrument from direct lighting so that the actual measurement surface lighting is no more than 200 lx can improve measurement accuracy and repeatability.

The temperature and humidity tolerances for the sample holding and measurement environments apply specifically to the vicinities in which the samples are held and measured. Operational fluctuations, operational uniformity and uncertainty of measurement shall be contained within the stated tolerances in those vicinities.

The measurement environment and sample holding environment, with respect to temperature, percentage relative humidity, ozone and light levels, and with respect to fluctuations and uniformity shall be reported in the test report.

The CIE colour coordinates of the D_{min} patch (unprinted paper) shall be measured using ISO 13655 measurement conditions for the relative spectral power distribution of the flux incident on the specimen surface. The conditions are chosen to be relevant to the characteristics being investigated. White backing is recommended in accordance with ISO 13655. Report the backing used or report the material opacity, according to ISO 2471, such that backing has no influence on the measurement. Measurement conditions shall be consistent throughout the test process. Conforming to ISO 13655, calculated tristimulus values and corresponding CIELAB values shall be computed using the illuminant and standard observer conditions applicable to the material under test.

NOTE 4 With completely opaque materials such as the aluminium substrate used in outdoor testing, the backing has no relevance.

Optical densities shall be measured according to ISO 5-3, with the relative spectral power distribution of the flux incident on the specimen surface conforming to CIE illuminant A, ISO 13655 measurement condition applicable to the characteristics being investigated, and spectral products conforming to Status A or Status T density, as appropriate for the material under test.

White backing is recommended in accordance with ISO 5. The ISO 5 standard reflection density shall be used as defined in ISO 5-4, allowing either annular influx mode or annular efflux mode. Either white or black backing is allowed. Report the backing used. Measurement conditions shall be consistent throughout the test process.

NOTE 5 When testing in accordance with an image life specification standard, then either standard status A or status T density is selected according to that specification standard.

A single measurement instrument shall be used for all of the measurements taken pertaining to a particular test. For example, initial patch values of a test target print and subsequent degraded patch values of that particular test target print shall be measured using the same measurement instrument. Replicate prints may be measured on separate measurement instruments as long as each is consistently measured on the same instrument used for its initial readings. According to best practice, in the case of equipment failure the test should be invalidated. A replacement instrument with a known offset, determined for the test measurement conditions and materials such as those being measured, may be used when the original instrument is not available. In this case, all measurements shall be corrected with the known offset.

NOTE 6 It is useful to retain an identical set of print samples for comparison so that the instrument offsets can be measured later if needed. These print samples are measured together with the test samples prior to ageing and then stored in a sealed bag in a freezer while the test samples are aged. Offset measurements from materials matched to those under test are preferred to measurements using BCRA tiles. See ISO 18920[25] for print storage methods.

7 Test methods — Thermal stability

7.1 General

7.1.1 “Free hanging” versus “sealed bag” methods

Long-term dark stability is evaluated by a series of tests carried out at several elevated temperatures at a particular relative humidity. Two test techniques, known as the “sealed bag” and the “free hanging” methods, are available for accelerated dark stability testing. These test methods, which can simulate two kinds of storage conditions, tend to give somewhat different results (see, for example, Reference [8]). In one storage condition, the photographic material is stored in a sealed container with very little air. Any substance released by the photographic material is trapped inside the container and can interact with the image or support. This situation is best simulated by the “sealed bag” method, in which preconditioned specimens are sealed in a moisture-proof bag from which most of the air has been expelled. An appropriate number of such bags are placed into ovens maintained at different test temperatures to permit specimen evaluation at periodic intervals. If this method is being used in conjunction with an image-life specification standard that defines endpoint criteria, evaluate at periodic intervals until at least one predetermined end point has been reached for the image-life parameters listed in the specification standard. The second storage condition, where images are kept in an open, unprotected environment (such as displayed print), is simulated by the "free hanging" method, in which the specimens are suspended in a relatively large test chamber at a sufficient distance from each other to ensure free access of the circulating air to all surfaces. In this free hanging condition, air circulation is controlled equally in the vicinity of all prints so that test results are consistent and repeatable.

Users of this document should be aware that the moisture content (by mass) of the specimens would differ somewhat with the two test methods, especially at increasingly high oven temperatures (see Reference [8]). With the "sealed bag" method, the moisture content within each bag will remain essentially constant, independent of oven temperature. With the "free hanging" method, however, the moisture content of the chamber environment will generally increase as the temperature of the ovens is increased at constant relative humidity. The influence of these differences on specimen moisture content and of the glass transition temperature of the gelatine emulsion or other binder on predictions of ageing behaviour may vary depending on the photographic material, the range of oven temperatures used, and the selected relative humidity value. If it is suspected that these differences could have a significant impact on fading and/or staining behaviour with a particular photographic material, it may be useful to conduct tests with both methods.

The choice of test method should be based on the known properties of the photographic materials being evaluated and the expected storage conditions of these materials. The choice of test method shall be reported.

7.1.2 Humidity effects

At relative humidity above 50 % RH, misleading results may be obtained, especially at the high temperatures used in accelerated tests, because of significant changes in the physical and/or chemical properties of some components of photographic imaging layers. For example, photographic gelatine changes from a solid to a gel state (glass transition temperature, T_g) at about 50 °C and 50 % RH. In the gel state, the structure and distribution of the image colourants may change with consequent changes in spectral absorption and/or covering power. An example of this is the smearing or bleeding of colourants in some dye-based inkjet systems, which is manifested as an initial density gain prior to fading that occurs at temperature and humidity combinations above the glass transition temperature (see Reference [10]). This can cause changes in hue, colour density, or both. This multiple mechanism may come into play only in accelerated ageing tests and, if so, precludes accurate predictions of ageing behaviour under normal storage conditions. Furthermore, ferrotyping and other physical defects may be induced at elevated temperatures and humidity.

7.1.3 Testing of low glass transition temperature products

Disproportionate increases or decreases in density values and/or pronounced changes in the appearance of the test specimens usually indicate the deleterious effects of high temperature treatment. Data derived from such specimens should be excluded from the computation of the test results if this results in non-linearity of the Arrhenius treatment as illustrated in Annex A. Exceeding the T_g of a material can in some (but not all) cases result in such non-linearity. In the case of such non-linearity, this document requires the use of lower temperatures and longer times to do the analysis.

While outside the scope of this document, other options exist for testing materials with limited T_g ranges without having to resort to extremely long, low temperature tests. The constant dew point method has been applied in some of these situations (see References [11], [12] and [13]).

7.1.4 Concerns around the effects of atmospheric pollutants

The major destructive influences on inkjet, electrophotographic and thermal dye diffusion images are heat, humidity, atmospheric gases and light exposure. Therefore it is prudent to separate these effects as much as possible into their individual components. Recent work has shown that for those