INTERNATIONAL STANDARD

ISO 18936

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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

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

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 18936 was prepared by Technical Committee ISO/TC 42, *Photography*.

Introduction

This International Standard 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 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 other 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 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 keeping 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; treatment of some chromogenic materials at temperatures above 80 °C and 60 %RH may cause loss of incorporated high-boiling solvents and abnormal image degradation; and 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 the bibliography). In general, photographic materials tend to undergo dramatic changes at relative humidities above 60 % (especially at the high temperatures employed in accelerated tests) owing to changes in the physical properties of gelatine and other binder materials. Lower maximum relative humidities 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 International Standard 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 chromogenic, silver dye-bleach, dye transfer, dye-diffusion-transfer “instant” systems and similar systems. The test method specified in this International Standard 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

ISO 11664-4, *Colorimetry — Part 4: CIE 1976 L*a*b* Colour space*

ISO 18911, *Imaging materials — Processed safety photographic films — Storage practices*

ISO 18913, *Imaging materials — Permanence — Vocabulary*

ISO 18920, *Imaging materials — Reflection prints — Storage practices*

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

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

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

ISO 18944, *Imaging materials — Reflection colour photographic prints — Test print construction and measurement*[1)]

3 Terms and definitions

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

3.1
operational control point
set point for equilibrium conditions measured at sensor location(s) in an exposure device

[ASTM G 113]

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1) To be published.

3.2
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 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.

[ASTM G 113]

3.3
operational uniformity
range around the operational control point for measured parameters within the intended exposure area within the limits of intended operational range

[ASTM G 113]

3.4
uncertainty (of measurement)
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could be reasonably attributed to the measurand

NOTE 1 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 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 It is understood that the result of the measurement is the best estimate of the value of the measurand, 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.

[ASTM G 113]

4 Requirements

This International Standard 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. Conversion of data obtained from these methods for the purpose of making public statements regarding product life shall be in accordance with the applicable International Standard(s) for specification of print life.

The test methods in this International Standard may be useful as stand-alone test methods for comparison of the stability of image materials with respect to one specific failure mode. Data from the test methods of this International Standard 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 International Standard, when reported in compliance with the reporting requirements of this International Standard. 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 International Standard makes use of the 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 International Standard 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 along with requirements and recommendations for sample preparation. Applicable International Standard(s) for specification of print life may require the use of specific targets. Other recommendations for sample preparation are contained in ISO 18909.

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 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. Ozone sensitivity is determined in accordance with ISO 18941 and ISO 18944. A material that is not sensitive to ozone shall have demonstrated no measurable D_{min} 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 2 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 condition M0 for the relative spectral power distribution of the flux incident on the specimen surface. 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 CIE illuminant D50 and the CIE 1931 standard colorimetric observer (often referred to as the 2° standard observer).

NOTE 3 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 M0, 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. Use ISO 5 standard reflection density 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 4 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 5 It is useful to retain freezer check print samples of the measurement materials so that instrument offsets can be measured if needed. Offset measurements from materials matched to those under test are preferred to measurements using BCRA tiles. Refer to ISO 18920 for print storage methods.

7 Measured attributes

7.1 Definition of density attributes

The symbol for measured density is d.

7.2 Density attributes to be measured

The following Status A or Status T densities of the specimens shall be measured before and after the treatment interval.

a) $d\mathrm{N(R)}_t$, $d\mathrm{N(G)}_t$, $d\mathrm{N(B)}_t$

the red, green and blue Status A or Status T densities of neutral patches that have been treated for time t, where t takes on values from 0 to the end of the test;

b) $d\mathrm{C(R)}_t$, $d\mathrm{M(G)}_t$, $d\mathrm{Y(B)}_t$

the red, green and blue Status A or Status T densities of cyan, magenta and yellow colour patches that have been treated for time t, where t takes on values from 0 to the end of the test,

c) $d\mathrm{R(G)}_\mathrm{t}$, $d\mathrm{R(B)}_\mathrm{t}$, $d\mathrm{G(R)}_\mathrm{t}$, $d\mathrm{G(B)}_\mathrm{t}$, $d\mathrm{B(R)}_\mathrm{t}$, $d\mathrm{B(G)}_\mathrm{t}$

the red, green and blue Status A or Status T densities of the composite secondary R, G, B colour patches that have been treated for time t, where t takes on values from 0 to the end of the test.

7.3 Definitions of colourimetry terms

L* is CIELAB lightness, a* and b* are the CIELAB a* and b* coordinates respectively, as defined in ISO 11664-4.

7.4 Colourimetry values to be measured

The following colourimetry values of the specimens, prepared as described in Clause 5, shall be measured before and after the treatment interval.

L*t, a*t, b*t

The lightness, red-green, and blue-yellow colour coordinates for the unprinted areas of specimens (paper white) that have been treated for time *t*, where *t* takes on values from 0 to the end of the test.

8 Calculations and computations

8.1 Computation of densitometric attributes

The calculations given in 8.2 to 8.9 shall be performed for patches with initial densities of 0,5, 1,0 and 1,5. Other starting densities may be used in addition, depending on the service needs of the specific product being tested.

8.2 Density change in d_{min} patches

a) Red density change: $\Delta d_{\mathrm{min}}(\mathrm{R})_t = d_{\mathrm{min}}(\mathrm{R})_t - d_{\mathrm{min}}(\mathrm{R})_0$

b) Green density change: $\Delta d_{\mathrm{min}}(\mathrm{G})_t = d_{\mathrm{min}}(\mathrm{G})_t - d_{\mathrm{min}}(\mathrm{G})_0$

c) Blue density change: $\Delta d_{\mathrm{min}}(\mathrm{B})_t = d_{\mathrm{min}}(\mathrm{B})_t - d_{\mathrm{min}}(\mathrm{B})_0$

8.3 Percent density change in pure primary colour patches

a) Cyan patch: $\%\Delta d\mathrm{C}(\mathrm{R})_t = [(d\mathrm{C}(\mathrm{R})_t - d\mathrm{C}(\mathrm{R})_0) \div d\mathrm{C}(\mathrm{R})_0] \times 100$

b) Magenta patch: $\%\Delta d\mathrm{M}(\mathrm{G})_t = [(d\mathrm{M}(\mathrm{G})_t - d\mathrm{M}(\mathrm{G})_0) \div d\mathrm{M}(\mathrm{G})_0] \times 100$

c) Yellow patch: $\%\Delta d\mathrm{Y}(\mathrm{B})_t = [(d\mathrm{Y}(\mathrm{B})_t - d\mathrm{Y}(\mathrm{B})_0) \div d\mathrm{Y}(\mathrm{B})_0] \times 100$

8.4 Percent density change in secondary (mixed) colour patches

a) Magenta in Red patch: $\%\Delta d\mathrm{R}(\mathrm{G})_t = [(d\mathrm{R}(\mathrm{G})_t - d\mathrm{R}(\mathrm{G})_0) \div d\mathrm{R}(\mathrm{G})_0] \times 100$

b) Yellow in Red patch: $\%\Delta d\mathrm{R}(\mathrm{B})_t = [(d\mathrm{R}(\mathrm{B})_t - d\mathrm{R}(\mathrm{B})_0) \div d\mathrm{R}(\mathrm{B})_0] \times 100$

c) Cyan in Green patch: $\%\Delta d\mathrm{G}(\mathrm{R})_t = [(d\mathrm{G}(\mathrm{R})_t - d\mathrm{G}(\mathrm{R})_0) \div d\mathrm{G}(\mathrm{R})_0] \times 100$

d) Yellow in Green patch: $\%\Delta d\mathrm{G}(\mathrm{B})_t = [(d\mathrm{G}(\mathrm{B})_t - d\mathrm{G}(\mathrm{B})_0) \div d\mathrm{G}(\mathrm{B})_0] \times 100$

e) Cyan in Blue patch: $\%\Delta d\mathrm{B}(\mathrm{R})_t = [(d\mathrm{B}(\mathrm{R})_t - d\mathrm{B}(\mathrm{R})_0) \div d\mathrm{B}(\mathrm{R})_0] \times 100$

f) Magenta in Blue patch: $\%\Delta d\mathrm{B}(\mathrm{G})_t = [(d\mathrm{B}(\mathrm{G})_t - d\mathrm{B}(\mathrm{G})_0) \div d\mathrm{B}(\mathrm{G})_0] \times 100$

8.5 Percent density change in a composite neutral patch

a) Cyan in neutral patch: $\%\Delta d\mathrm{N}(\mathrm{R})_t = [(d\mathrm{N}(\mathrm{R})_t - d\mathrm{N}(\mathrm{R})_0) \div d\mathrm{N}(\mathrm{R})_0] \times 100$

b) Magenta in neutral patch: $\%\Delta d\mathrm{N}(\mathrm{G})_t = [(d\mathrm{N}(\mathrm{G})_t - d\mathrm{N}(\mathrm{G})_0) \div d\mathrm{N}(\mathrm{G})_0] \times 100$

c) Yellow in neutral patch: $\%\Delta d\mathrm{N}(\mathrm{B})_t = [(d\mathrm{N}(\mathrm{B})_t - d\mathrm{N}(\mathrm{B})_0) \div d\mathrm{N}(\mathrm{B})_0] \times 100$

8.6 Colour balance shift in a composite neutral patch

Contrast and colour balance distortions brought about by differential fading of the three image colourants can result in significant visually degrading effects. These can be measured as shifts in colour balance from highlights to shadows and 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.

Neutral colour balance shift is calculated as the difference in percentage change between any two primary colours of a neutral patch. The percentage change of individual primary colours in a neutral patch is defined in 8.5.

a) Cyan-magenta shift: $\%\Delta d\mathrm{N(R\text{-}G)}_t = |\%\Delta d\mathrm{N(R)}_t - \%\Delta d\mathrm{N(G)}_t|$

b) Magenta-yellow shift: $\%\Delta d\mathrm{N(G\text{-}B)}_t = |\%\Delta d\mathrm{N(G)}_t - \%\Delta d\mathrm{N(B)}_t|$

c) Yellow-cyan shift: $\%\Delta d\mathrm{N(B\text{-}R)}_t = |\%\Delta d\mathrm{N(B)}_t - \%\Delta d\mathrm{N(R)}_t|$

8.7 Colour balance in secondary (mixed) colour patches

Secondary colour balance shift is calculated as the difference in percentage change between the two primary colours of each secondary colour patch. The percentage change of the individual primary colours in each secondary colour patch is defined in 8.4.

a) Cyan-magenta shift in Blue patch: $\%\Delta d\mathrm{B(R\text{-}G)}_t = |\%\Delta d\mathrm{B(R)}_t - \%\Delta d\mathrm{B(G)}_t|$

b) Magenta-yellow shift in Red patch: $\%\Delta d\mathrm{R(G\text{-}B)}_t = |\%\Delta d\mathrm{R(G)}_t - \%\Delta d\mathrm{R(B)}_t|$

c) Yellow-cyan shift in Green patch: $\%\Delta d\mathrm{G(B\text{-}R)}_t = |\%\Delta d\mathrm{G(B)}_t - \%\Delta d\mathrm{G(R)}_t|$

8.8 Colour balance in d_{min} patches by densitometry

a) Cyan-magenta shift: $\Delta d_{\mathrm{min}}(\mathrm{R - G})_t = \Delta d_{\mathrm{min}}(\mathrm{R})_t - \Delta\, d_{\mathrm{min}}(\mathrm{G})_t$

b) Magenta-yellow shift: $\Delta d_{\mathrm{min}}(\mathrm{G - B})_t = \Delta\, d_{\mathrm{min}}(\mathrm{G})_t - \Delta\, d_{\mathrm{min}}(\mathrm{B})_t$

c) Yellow-cyan shift: $\Delta d_{\mathrm{min}}(\mathrm{B - R})_t = \Delta\, d_{\mathrm{min}}(\mathrm{B})_t - \Delta d_{\mathrm{min}}(\mathrm{R})_t$

8.9 Colour balance in d_{min} patches by colourimetry

Colour balance in the d_{min} patches is measured using the following equation

$$\Delta E^*_{ab} = \sqrt{(L^*_t - L^*_0)^2 + (a^*_t - a^*_0)^2 + (b^*_t - b^*_0)^2}$$

where L*, a* and b* are the colour coordinates of the d_{min} patch at the initial time 0 and at time t, as defined by ISO 11664-4.

9 Test methods — Thermal stability

9.1 General

9.1.1 “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 moistureproof 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 until at least one predetermined end point has been reached for the image-life parameters listed in the specifications 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 International Standard should be aware that the moisture content (by weight) 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 employed, 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.

9.1.2 Humidity effects

At relative humidities above 50 %RH, misleading results may be obtained, especially at the high temperatures employed 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 humidities.

9.1.3 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 illustrated in Annex B. 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 International Standard requires the use of lower temperatures and longer times to do the analysis.

While outside the scope of this International Standard, 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]).

9.1.4 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 materials studied (and especially so for the porous inkjet media) the effects once thought to be light-fade reciprocity failure are actually dark interactions of atmospheric pollutants with the prints. (See Reference [15]). Separate testing for sensitivity to atmospheric pollutants shall be conducted following the methods specified in ISO 18941.

Because of the potential sensitivity to air pollution for some imaging materials, the tests described in this standard shall be run in an ozone-free condition, which is defined as = < 2 nl/l average ozone concentration over any 24 h period. While the sealed bag method is relatively immune to atmospheric pollutants, there is potentially a concern in the free hanging method. One way to comply with the requirement for the ozone-free condition is to use humidified environmental chambers in a laboratory with an average ozone concentration of < 2 nl/l over any 24 h test period. An alternative method is to use humidified environmental chambers with an average ozone concentration of < 2 nl/l over any 24 h test period.

9.2 Test methods and equipment

9.2.1 Temperature

At least four different temperatures shall be used at any one of the test conditions described in 9.2. The test temperature range shall be at least 20 °C. When the highest temperature possible for linear performance (see 9.1.3) with a particular material is less than or equal to 55 °C, then the temperature range can be 15 °C, provided that four points are still tested per the Arrhenius method in ISO 18924. The temperature intervals shall be approximately equal, e.g. 55 °C, 65 °C, 75 °C and 85 °C.

The preferred air temperature shall be according to the test method. The air temperature shall be maintained and controlled throughout testing with an operational fluctuation within ± 2,0 °C of aim. The 24 h running average of the operational fluctuation, sampled at least every 15 min, shall be within ± 1,0 °C of aim. The running average shall not include the test condition transition time of at most 1 h after operation at the test condition is initiated. Each time the chamber aim temperature is changed, the chamber shall be recalibrated for temperature using a reference calibration standard, such as a chilled mirror hygrometer. Operational uniformity of the equipment at the test conditions shall be evaluated prior to test start and shall be within ± 2,0 °C of aim. Regions of the test chamber shall be selected for use to comply with the required operational uniformity conditions. If the running average of the operational fluctuation does not meet the requirement, it shall be documented and explained.

9.2.2 Relative humidity

Because the effects of humidity on image stability can differ markedly from one product to another, it is useful to evaluate its effect. This is done by means of a temperature test series carried out at different relative humidities. If the relative humidity during storage is expected to be significantly lower than 50 %RH, such as when stored in accordance with some conditions specified in ISO 18911, ISO 18920 or in an arid climate, or significantly higher, as in a tropical climate, the relative humidity selected for the test should correspond to the storage conditions. Such tests are often conducted at conditions of various %RH levels, such as 20 %RH to pick up low humidity effects and 70 %RH to pick up high humidity effects.

The preferred level of relative humidity shall be 50 %RH at the control temperature. Other levels may be used, such as 20 %RH and 70 %RH, where such levels reflect actual product use conditions. In all cases, the relative humidity test conditions shall be reported. The relative humidity shall be maintained and controlled throughout testing with an operational fluctuation within ± 6 %RH of aim. The 24 h running average of the operational fluctuation, sampled at least every 15 min, shall be within ± 2 %RH of aim. The running average shall not include the test condition transition time of at most 1 h after operation at the test condition is initiated. Operational uniformity of the equipment at the test conditions shall be evaluated prior to test start and shall be within ± 3 %RH of aim, at a constant temperature. Regions of the test chamber shall be selected for use to comply with the required operational uniformity conditions. If the running average of the operational fluctuation does not meet the requirement, it shall be documented and explained.

Each test chamber shall be calibrated for relative humidity control and measurement accuracy by using a chilled mirror hygrometer or other type of measurement device calibrated and traceable to a national standards bureau suitably responsible for certifying reference weights and measures. The calibration shall include the full temperature and relative humidity ranges that are to be used in the ensuing test processes. A check of the calibration shall be performed when there is any indication of sensor failure. Ongoing use of redundant sensors is recommended so that sensor integrity can be ascertained.

9.2.3 Number of specimens

The specimens should be representative of the products and modes of processing to be evaluated.

NOTE Paper materials used in testing should be obtained fresh from sealed packaging. Samples should be handled only with gloves. Exposure to ambient light should be minimized during sample measurements.

These specimens are measured before incubation and at predetermined intervals thereafter, as the specimens are withdrawn from the temperature/humidity-controlled ovens. While the same specimens are generally used throughout the test period in the free hanging method, there may be situations where it is advantageous to put multiple samples into one chamber, discarding each one after it has reached its intended exposure increment.

Normally, measurements should be made at five or more time intervals during a period that is long enough for fading and/or staining to reach beyond one or more selected end points. Generally, the required time intervals at the lower temperatures can be deduced from the fading and staining rates observed at the higher temperatures.

It is suggested that additional tests with identical specimens be repeated at different times to provide an indication of the repeatability of the test procedures and testing equipment.

9.2.4 Free hanging method at constant relative humidity

For each temperature condition described in 9.2.1, samples of all materials shall be hung, for example, by clips or rods such that they are freely exposed to the atmosphere within a temperature and humidity-controlled chamber. Weights may be attached to the lower end of the samples, if necessary, to prevent excessive curl due to humidity or to prevent excess movement of the samples if air is moving very fast in the chamber. Specimens shall be free hanging in air of controlled temperature and relative humidity.

Recirculating forced-air environmental chambers shall be used. Airflow shall be consistent throughout the print hanging area, and at the various temperatures. Airflow measurements shall be read in appropriate locations in the chamber. One temperature- and humidity-controlled chamber is required for each temperature condition. However, if there is a problem with gas phase cross-contamination of samples, some samples may have to be segregated in their own chamber. A single set of targets can be run using this method. Samples are removed for reading and generally replaced after readings have been made.

NOTE Airflow may be an issue with respect to variability in unprinted sample yellowing. After each interval measurement, samples can be returned to the chamber in another location to minimize the effects of airflow variation around the chamber. This can also be a factor with use of multiple chambers (see Reference [18]).

The use of desiccators containing aqueous solutions as humidity chambers has several practical difficulties, and the aqueous solutions could lead to chemical contamination of the test specimens. For this reason, desiccators shall not be used for the tests specified in this International Standard. The atmospheric requirements can be obtained with temperature- and humidity-controlled environmental chambers of the type in which the relative humidity is maintained by controlled contact of recirculated air with humidifying water or controlled injection of humidified air.

Care should be taken about the sensitivity of some samples to ambient ozone levels. Procedures to deal with this are covered in 9.1.4.

9.2.5 Sealed bag method (constant moisture content)

Recirculating forced-air ovens of controlled temperature shall be used. Because control of relative humidity within the test ovens is not necessary, dry ovens (which are much less expensive than humidity-controlled ovens) may be used for the heat-sealed bag method.

In addition to the test specimens used for measurements, D_{min} printed or processed media of the same kind shall be used for fillers for test media for heat-sealed bag incubations. Unprinted digital output can be used for fillers for digitally generated output tests. The samples and fillers for each material shall be conditioned at 23 °C ± 2 °C and the relative humidity of the test. Moisture conditioning shall sequentially follow the dry down/cure period that is specified in 5.1. The moisture conditioning period shall be seven days. If the %RH condition for the test is 50 %RH, then a moisture conditioning period beyond the dry down/cure period shall still be required.

After conditioning, the sample stack and fillers shall be inserted into a bag consisting of a layer of polyethylene inside coated with a layer of aluminium foil. The outside layer may be one of a number of substances, including paper, polypropylene, or polyamide. High quality bags shall be used to ensure that the test is not compromised by contaminants off-gassing from the bag material. The air shall be squeezed out as much as possible, and the bag shall be sealed with a hot dry iron or an impulse sealer. Excess areas of bag shall be folded over and this package shall be inserted into a second bag. The outside bag shall have as much air squeezed out as possible and will then be sealed with a hot, dry iron or impulse sealer. This process shall be repeated for each of the replicate samples. If sticking is a problem such that test measurements are compromised at the required test conditions, then 50 μm to 75 μm thick polytetrafluoroethane (PTFE) may be used to interleave samples rather than the filler material as a separate test. Results using filler media and PTFE cannot be compared.

A separate bag is needed for each of the multiple density measurements to be made during the entire test period, because specimens that have been withdrawn from an oven and removed from a bag shall not be re-bagged and further incubated. The total number of specimens and bags required to evaluate a particular product will depend on the number of withdrawals from the ovens for measurement. This number will be determined by the inherent stability of the product, the number of test temperatures and the relative humidities employed. Withdrawal intervals of hours and days often are appropriate for the highest temperatures, and weeks or months for the lower temperatures. Once specimens have been removed from a bag for density measurements, the specimens shall not be subjected to further incubation.

9.3 Computation of dark stability

The mathematical procedures for estimating image life by the Arrhenius method are shown in Annex B. However, this can only be completed when used with the selected end points, for example those specified in the appropriate print life standard, such as an image specification standard (see Clause 4). Alternative end points may be used for other applications of this International Standard. Note that the end points are to be qualified as sufficiently above the noise of the test.

10 Test report

10.1 General reporting requirements

Reporting based solely on this test method shall be restricted to reporting the specific thermal stability test result, and shall include reporting of the test procedure (e.g. sealed bag, free hanging), the humidity (%RH), the temperature and the test time duration. For the free hanging test case, both the conditioning %RH and the test %RH shall be reported. For the sealed bag test case, the conditioning %RH shall be reported. Arrhenius extrapolations using the conditions in this test method deal only with thermal stability and exclude the potential effects of other factors such as gas fading that may also be present in real-world conditions.

Users are cautioned that results from this test method apply only to the specific system tested. For example, in inkjet systems, a specific ink used with a specific paper may have very different results from another. Test reporting shall include this disclaimer.

10.2 Test reporting

The results of these tests are reported as cumulative exposure (temperatures and time) to reach the observed optical densities, together with the percentage of optical density losses, or the amount of densitometric and/or colourimetric change observed for a given cumulative exposure.

The report of test results shall include the following information.

- The target patch encoding values of the patches selected for monitoring in the test, and the corresponding initial densities (i.e. 1,0) of the neutral and colour patches; the number of duplicate test specimens included in the test.
- The backing used during measurement or the material opacity according to ISO 2471.
- For digital output samples, the printer model, printer driver version, printer driver settings, printer front panel settings, the name of the host application used in generating the print, and the colour controls selected in that application; the cartridge configuration/ink/donor or colourant used (manufacturer’s name

and part number); the paper used (manufacturer's name and model number); and any other necessary information, such that the print file can be reproduced by another user of this International Standard. For silver-halide based samples, the processing conditions (i.e. chemicals, procedures). In all cases, any post-processing treatments that may have been applied to the prints.

— The test method (constant RH or constant moisture) and conditions that were actually used (i.e. the actual temperature, relative humidity, measured airflow, and test concentration and control aim level). If the actual test conditions deviate from the nominal conditions specified in this International Standard, then an explanation shall be provided.

— Duration of the test, including the extent and level to which the test was conducted.

NOTE As a minimum, the extent and level shall be at least long enough such that a fade signal (loss or gain) can be statistically separated from test noise.

— The experimentally derived Arrhenius equation and some measure of the "goodness of fit" of the data.

— Results of the Arrhenius extrapolation such as years to end point, excluding reporting as image life.

Annex A
(informative)

A method for interpolation

Often there will not be a step on a properly designed and printed test target that is of exactly the desired density. Interpolation between two neighbouring density patches can be used to predict the values for the exact desired starting density. For example, the densities of the two steps nearest to 1,0 may be used to calculate the desired density by linear interpolation. After each fading time, the same coefficient is used for interpolating the density after fading.

First, on the unfaded strip, the step with the density d_1 just below 1,0 and the step with the density d_2 just above 1,0 are chosen (see Figure A.1). After fading, these two steps will have reached the densities $d_1(t)$ and $d_2(t)$. The density $d(t)$ of the initial $d = 1{,}0$ is then estimated through linear interpolation:

$$d_t = d_{1(t)} + [d_{2(t)} - d_{1(t)}]\alpha$$

where

$$\alpha = \frac{1{,}0 - d_{1(t=0)}}{d_{2(t=0)} - d_{1(t=0)}}$$

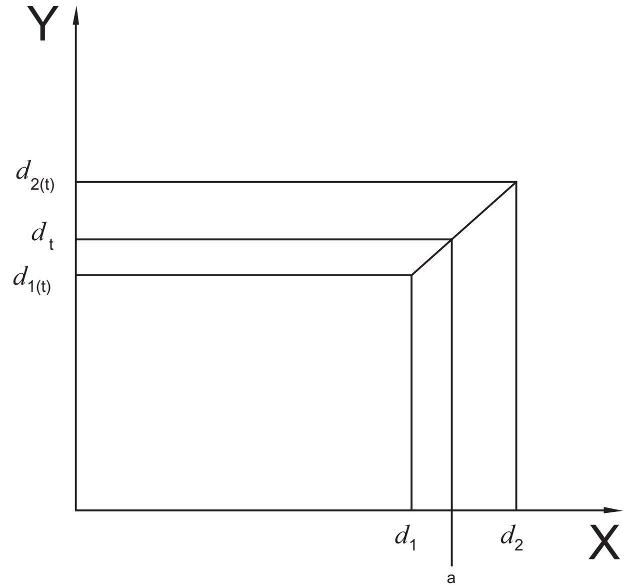


Figure A.1 — Interpolation of a test target starting density patch

Annex B
(informative)

Illustration of Arrhenius calculation for dark stability

B.1 Plot of colour fading

This annex illustrates the Arrhenius calculation using as an example the fading of a yellow colour patch and the resulting densities after incubation at 60 °C and 50 %RH. The required density parameters can be found in Table B.1 for generating the fading curve at 60 °C. They are as follows:

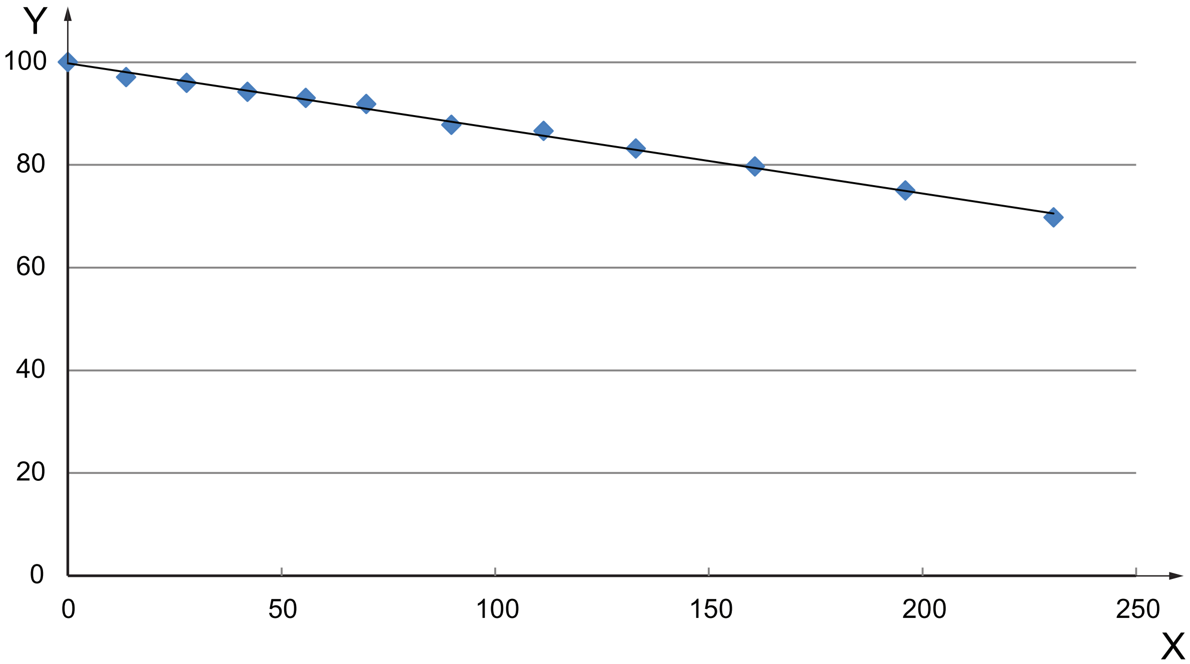
- the time, t, in the oven ranged from 0 d to 231 d;
- dY (B)t (see 7.2);
- [100 - %ΔdY(B)t], the percentage blue density retention of the yellow colour patch at time t (see 8.3).

Table B.1 — Densitometry data for reflection material in a 60 °C/50 %RH oven

Time t (days)	dY(B)t	100 - %ΔdY(B)t
0	1,02	100
14	0,99	97
28	0,98	96
42	0,96	94
56	0,95	93
70	0,94	92
90	0,90	88
112	0,89	87
133	0,85	83
161	0,82	80
196	0,76	75
231	0,71	70

Densitometry of the yellow patches (dY(B)t) gives densities to blue light at each of the times t. These densities include both the density due to the presence of the yellow colourant and also the blue density of the support and other miscellaneous colourants.

[100 - %dY(B)t] is plotted in Figure B.1 against the time, t, in days. A smooth curve is then drawn manually through the points. The same procedure is applied to the data from all temperatures. From these plots, one can interpolate the times required for the fading or decreasing of the original density dY(B)o to reach a specified value, such as 30 % loss (70 % retention of the original density). In this example, the values of the time for 70 % retention are determined from the plot (Figure B.1). These times, t, at each temperature are then used to make the Arrhenius plot.



Key

x incubation (days)

y density retention (%)

Figure B.1 — Density versus time of incubation (at 60 °C)

B.2 Computer implementation of the Arrhenius method

The Arrhenius equation (see Reference [4]) describes an empirical relationship between absolute temperature (T, in degrees Kelvin) and the rate constant (k) for a chemical reaction and can be written in the form In $k = (-E_a/RT) +$ In A, where R is a universal constant and E_a and A are constants characteristic of the reaction. A plot of In k versus $1/T$ is expected to be linear, and over a reasonable temperature range, the equation has been confirmed as a good approximation for a large number of both simple and complex chemical processes (see Reference [18]). In applications related to this International Standard, it is usual to plot the log of the times necessary to reach a specified density (e.g. a 30 % density loss) against values of inverse temperature; this generates a plot with a positive slope (E_a/R) that can be extrapolated to estimate the time to reach the chosen density change at a temperature of interest, e.g. 23° C (see Figure B.2).

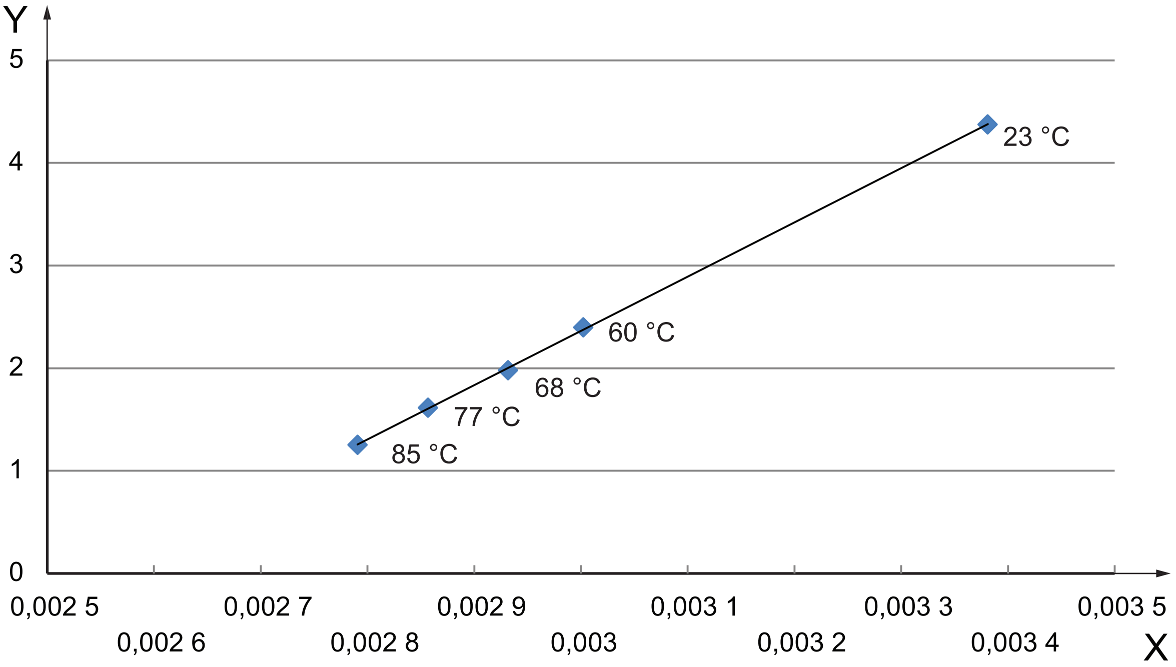
Computerization of this methodology not only permits a convenient handling of large amounts of data, but also can improve the quality of the extrapolated estimates by providing an unbiased best-fit line, as well as estimates of errors for the extrapolated values. Commercial computer software, such as Excel, JMP, SAS, S-Plus and others can be used to obtain such fits, as well as provide a plot of the data for visual confirmation. Most simply, the software can be used to calculate the reciprocal of the absolute temperature (K^{-1}) and the corresponding log of the time for a particular density loss from, respectively, the measured temperature and the corresponding density change [e.g. $\%\Delta d\mathrm{Y(B)}t$] (see Table B.2 as an example).

Table B.2 — Calculated parameters of reciprocal temperature and log of days for 30 % fade.

T (°C)	T (1/K)	Time for 30 % loss[a]	Log time
85	0,00279	18	1,26
77	0,00286	40	1,60
68	0,00293	95	1,98
60	0,00300	228	2,36

[a] Time to lose 30 % in density from an initial density of 1,00. Thirty-percent loss is a value used strictly for illustrative purposes only.

If one creates a plot of the log of time versus reciprocal temperature, the best-fit line through these data provides a means of calculation for the time to 30 % loss in density at 296 K or 23 °C (see Figure B.2). Extrapolating the points in this plot through linear regression gives a prediction of approximately 60 years for the colourant to lose 30 % of its density at 23 °C.



Key

x 1/*T* (1/Kelvin)

y log time (days)

Figure B.2 — Plot of log days to 30 % density loss versus reciprocal temperature (Arrhenius plot)

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