IEC TS 60216-7-1

Edition 1.0 2015-03

TECHNICAL SPECIFICATION

Electrical insulation materials – Thermal endurance properties – Part 7-1: Accelerated determination of relative thermal endurance using analytical test methods (RTE_A) – Instructions for calculations based on activation energy

IEC TS 60216-7-1:2015-03(en)

IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
Fax: +41 22 919 03 00
info@iec.ch
www.iec.ch

About the IEC
The International Electrotechnical Commission (IEC) is the leading global organization that prepares and publishes International Standards for all electrical, electronic and related technologies.

About IEC publications
The technical content of IEC publications is kept under constant review by the IEC. Please make sure that you have the latest edition, a corrigenda or an amendment might have been published.

IEC Catalogue - webstore.iec.ch/catalogue
The stand-alone application for consulting the entire bibliographical information on IEC International Standards, Technical Specifications, Technical Reports and other documents. Available for PC, Mac OS, Android Tablets and iPad.

IEC publications search - www.iec.ch/searchpub
The advanced search enables to find IEC publications by a variety of criteria (reference number, text, technical committee,…). It also gives information on projects, replaced and withdrawn publications.

IEC Just Published - webstore.iec.ch/justpublished
Stay up to date on all new IEC publications. Just Published details all new publications released. Available online and also once a month by email.

Electropedia - www.electropedia.org
The world's leading online dictionary of electronic and electrical terms containing more than 30 000 terms and definitions in English and French, with equivalent terms in 15 additional languages. Also known as the International Electrotechnical Vocabulary (IEV) online.

IEC Glossary - std.iec.ch/glossary
More than 60 000 electrotechnical terminology entries in English and French extracted from the Terms and Definitions clause of IEC publications issued since 2002. Some entries have been collected from earlier publications of IEC TC 37, 77, 86 and CISPR.

IEC Customer Service Centre - webstore.iec.ch/csc
If you wish to give us your feedback on this publication or need further assistance, please contact the Customer Service Centre: csc@iec.ch.

IEC TS 60216-7-1

Edition 1.0 2015-03

TECHNICAL SPECIFICATION

Electrical insulation materials – Thermal endurance properties – Part 7-1: Accelerated determination of relative thermal endurance using analytical test methods (RTE_A) – Instructions for calculations based on activation energy

INTERNATIONAL ELECTROTECHNICAL COMMISSION

ICS 19.020; 29.020; 29.035.01

ISBN 978-2-8322-2430-4

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

_____

ELECTRICAL INSULATION MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-1: Accelerated determination of relative thermal endurance using analytical test methods (RTE_A) – Instructions for calculations based on activation energy

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.
3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.
4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.
5) IEC itself does not provide any attestation of conformity. Independent certification bodies provide conformity assessment services and, in some areas, access to IEC marks of conformity. IEC is not responsible for any services carried out by independent certification bodies.
6) All users should ensure that they have the latest edition of this publication.
7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.
8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.
9) Attention is drawn to the possibility that some of the elements of this IEC Publication may be the subject of patent rights. IEC shall not be held responsible for identifying any or all such patent rights.

The main task of IEC technical committees is to prepare International Standards. In exceptional circumstances, a technical committee may propose the publication of a technical specification when

- the required support cannot be obtained for the publication of an International Standard, despite repeated efforts, or
- the subject is still under technical development or where, for any other reason, there is the future but no immediate possibility of an agreement on an International Standard.

Technical specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 60216-7-1, which is a technical specification, has been prepared by IEC technical committee 112: Evaluation and qualification of electrical insulation materials and systems.

The text of this technical specification is based on the following documents:

Enquiry draft	Report on voting
112/298/DTS	112/314/RVC

Full information on the voting for the approval of this technical specification can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 60216 series, published under the general title *Electrical insulating materials – Thermal endurance properties*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- transformed into an International standard,
- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

INTRODUCTION

The existing procedures of the IEC 60216 series for the evaluation of thermal endurance of an electrical insulation material can be time consuming. These methods are therefore of limited use during development of new materials or screening of existing products for use as a material in an electrical insulation. There is an important demand from industry for a rapid test method of relative thermal endurance (RTE) / temperature index (TI) and halving interval (HIC) to reduce project times and cost. A short-term test procedure for conventional thermal endurance characterization is proposed in IEC 60216-5 and a simplified approach to data processing is described in IEC 60216-8. Non-conventional methodology for thermal endurance characterization which can reduce further test times is considered in this technical specification.

The basic procedure is based on thermal analysis methods (DSC and TGA in particular, but not restricted to them) to evaluate the activation energy of the thermal degradation of the material. The activation energy is directly correlated with the HIC of the thermal endurance.

With this information, a single-point thermal endurance test, according to IEC 60216-1 and IEC 60216-5, at the highest temperature of those selected for the conventional thermal ageing procedure, is sufficient to calculate the temperature corresponding to a selected life, typically 20 000 h, i.e. an estimate of TI. However, due to the inherent uncertainty associated with this analytical approach, only RTE can be provided for material characterization. This is obtained performing the single-point thermal endurance test in the same conditions of temperature and environment as a reference material of known thermal endurance characteristics, i.e. TI and HIC.

The analytical test methods described in this technical specification may satisfy the demand of shortening the insulating material characterization procedure, if used with care and considering the restrictions these methods imply. At present, the universal applicability and the accuracy of these methods is not validated, thus a round robin test is required to provide an IEC standard based on these procedures. This part of IEC 60216 is therefore published as a technical specification.

A general assessment process of the procedures will be developed in other sub-parts of IEC 60216-7.

ELECTRICAL INSULATION MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-1: Accelerated determination of relative thermal endurance using analytical test methods (RTE_A) – Instructions for calculations based on activation energy

1 Scope

This technical specification describes the procedure for the evaluation of the thermal endurance of electrical insulating materials, based on thermal analysis methods for the evaluation of the activation energy of the thermal degradation reaction and a conventional life test providing a life point in the thermal endurance graph. The purpose of the test procedure is to estimate the relative temperature index (RTE).

Predictions of thermal endurance based on this procedure are limited to ageing reactions where one single reaction is predominant and directly correlated to the end-point criteria for a specific application.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 60085, *Electrical insulation – Thermal evaluation and designation*

IEC 60216-1, *Electrical insulating materials – Thermal endurance properties – Part 1: Ageing procedures and evaluation of test results*

IEC 60216-2, *Electrical insulating materials – Thermal endurance properties – Part 2: Determination of thermal endurance properties of electrical insulating materials – Choice of test criteria*

IEC 60216-5, *Electrical insulating materials – Thermal endurance properties – Part 5: Determination of relative thermal endurance index (RTE) of an insulating material.*

IEC 60216-8, *Electrical insulating materials – Thermal endurance properties – Part 8: Instructions for calculating thermal endurance characteristics using simplified procedures*

ISO 11357-6, *Plastics – Differential scanning calorimetry (DSC) – Part 6: Determination of oxidation induction time (isothermal OIT) and oxidation induction temperature (dynamic OIT)*

ISO 11358-2, *Plastics – Thermogravimetry (TG) of polymers – Part 2: Determination of activation energy*

ISO 11358-3, *Plastics – Thermogravimetry (TG) of polymers – Part 3: Determination of the activation energy using the Ozawa-Friedman plot and analysis of the reaction kinetics*

3 Terms, definitions and abbreviations

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
reaction rate
r
change of the concentration of a chemical entity as a function of time

[SOURCE: IUPAC “Goldbook”]

3.1.2
extent of reaction
ξ
progress of a chemical reaction equal to the number of chemical transformations

[SOURCE: IUPAC “Goldbook”]

3.1.3
rate of conversion
$\dot{\xi}$
time derivative of the extent of reaction

[SOURCE: IUPAC “Goldbook”]

3.1.4
order of reaction
n
indication of the number of entities affecting the macroscopic rate of reaction

[SOURCE: IUPAC “Goldbook”]

3.1.5
diagnostic property
p
property to which TI is related

Note 1 to entry: See definition in IEC 60216-1.

3.1.6
rate law
empirical differential rate equation, an expression for the rate of a particular reaction in terms of concentrations of chemical species

[SOURCE: IUPAC “Goldbook”]

3.1.7
reaction rate constant
k
proportionality factor k of a rate law

[SOURCE: IUPAC “Goldbook”]

3.1.8
Arrhenius equation
empirical exponential law relating reaction rate constant to reciprocal of absolute temperature

[SOURCE: IUPAC “Goldbook”]

3.1.9
activation energy (Arrhenius activation energy)
E_a
empirical parameter characterizing the exponential temperature dependence of the reaction rate constant

[SOURCE: IUPAC “Goldbook”]

3.1.10
pre-exponential factor
A
coefficient of the Arrhenius equation

[SOURCE: IUPAC “Goldbook”]

3.1.11
end-point
limit for a diagnostic property value based on which the thermal endurance is evaluated

3.1.12
time to end-point
failure time
time to reach the end-point or conventional failure

3.1.13
relative temperature endurance index
RTE
numerical value of the temperature in degrees Celsius at which the estimated time to end-point of the candidate material is the same as the estimated time to end-point of the reference material at a temperature equal to its assessed temperature index

Note 1 to entry: RTE_A is the relative temperature endurance index calculated through the analytical procedure.

3.1.14
temperature index
TI
numerical value of the temperature in degrees Celsius derived from the thermal endurance relationship at a time of 20 000 h (or other specified time)

Note 1 to entry: TI_A is the temperature index calculated through the analytical procedure.

[SOURCE: IEC 60050-212:2010, 212-12-11, modified according to IEC 60216-1].

3.1.15
halving interval
HIC
numerical value of the temperature interval in kelvin which expresses the halving of the time to end-point taken at the temperature equal to TI

Note 1 to entry: HIC_A is the halving interval calculated through the analytical procedure.

[SOURCE: IEC 60050-212:2010, 212-12-13, modified according to IEC 60216-1]

3.1.16
thermal endurance graph
graph in which the logarithm of the time to reach a specified end-point in a thermal endurance test is plotted against the reciprocal thermodynamic test temperature

[SOURCE: IEC 60050-212:2010, 212-12-10]

3.1.17
thermal endurance graph paper
graph paper having a logarithmic time scale as the ordinate, graduated in powers of ten (from 10 h to 100 000 h is often a convenient range) and values of the abscissa are proportional to the reciprocal of the thermodynamic (absolute) temperature

Note 1 to entry: The abscissa is usually graduated in a non-linear (Celsius) temperature scale oriented with temperature increasing from left to right.

3.2 Abbreviations

DSC	scanning calorimetry
FTIR	Fourier transform infrared
GC-MS	gas chromatography–mass spectrometry
HIC	halving interval
OIT	oxygen induction time
RTE	relative temperature endurance index
TGA	thermogravimetric analysis
TI	temperature index

4 General considerations

4.1 Thermal degradation kinetics

The general principles of IEC 60216 to determine the temperature index and halving interval are based on the implicit assumption of a first-order kinetic of the thermal degradation process of the insulation material. Only under these conditions the thermal endurance graph is linear and halving interval is independent of the concentration of the reactants.

It is a plausible assumption that the condition of an insulating material at the time of reaching the defined end-point criteria according to IEC 60216 is correlated to a certain conversion of the thermal degradation process. Therefore, by knowing the reaction mechanism and kinetics of the thermal degradation process of an insulation material, it should be possible to estimate the thermal endurance of an insulating material.

The most important mechanisms for the degradation of insulating materials are thermal oxidation, pyrolysis, and hydrolysis of the basic polymer. Unfortunately, from a theoretical point of view, none of these reactions can be considered a priori as reactions with first-order kinetics. Pyrolysis reactions follow in general zero-order kinetics, and oxidation and hydrolysis reactions are reactions of higher order because concentration of oxygen, respectively water, will determine the total reaction rate. The degradation reaction can be considered a heterogeneous reaction having the insulating material as the solid phase and the environmental atmosphere as the gas phase. Various processes will influence the total reaction rate, such as adsorption of reactants (oxygen, water) and desorption (reaction products), as well as diffusion of reactants and products in the solid and fluid phase. Only if one of these reactions is predominant, can the overall observable reaction rate follow first-order kinetics (“pseudo first-order”).

The most common method for the evaluation of the activation energy of a chemical reaction is the determination of the concentration of reactants and/or products as a function of time and

temperature. These experiments allow the identification of the order of the reaction and the activation parameters according to the Arrhenius theory.

NOTE 1 These experiments will not necessarily give information about the reaction on a molecular level, because the build-up of intermediate products with a short life time may not be observed if the reaction has not been fractionated into a series of elementary reactions.

NOTE 2 The Eyring theory of the activated complex gives a fundamental understanding of elementary reactions and the influence of the temperature and molecular statistics on the reaction rate. However, for first order reaction the Arrhenius model can be considered with good accuracy.

For some insulating materials, like polyolefin-based plastics, the thermal endurance is correlated to the concentration of stabilizers (anti-oxidant). The progressive consumption of the stabilizer is a cause of enhanced oxidation rate. The reaction of the stabilizer follows a first-order kinetics and is therefore an example where the use of the Arrhenius law for the prediction of the thermal endurance of these materials can give good results.

Methods based on the observation of the conversion process have been developed for the evaluation of the “kinetic triplet” (activation energy, pre-exponential factor, and rate law). However, it can be difficult and time consuming to investigate the rate law of chemical reactions by observing the variation of concentrations for reaction products, and the thermal analysis instruments can only provide general information about the total thermal conversion of a material, not the concentration of single reaction products or components.

4.2 Thermal analysis

The most common thermal analysis test methods for these investigations are differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Both methods allow both isothermal investigations and test runs with constant heating rates.

NOTE These technologies can be complemented by additional equipments for chemical analysis, e.g. FTIR spectroscopy, mass spectroscopy, or GC-MS, to validate evaluation of activation energy by thermal analysis.

To simplify and accelerate analytical test procedures, alternative mathematical framework, such as ISO 11358-2 and ISO 11358-3, has been developed to compute the kinetic triplet from conversional data of thermal analysis known as “isoconversional methods”. In general, a set of thermo analytical experiments with 3 to 5 different heating rates is required to estimate the activation energy for a defined rate of conversion, but isoconversional methods can also be used for isothermal runs.

Because for single step reactions the activation energy is independent of the degree of conversion, in this case this method provides a simple tool for activation energy calculation. In fact, repetitive application of this technique on test results of the same degree of conversion at various heating rates allows the calculation of the activation energy as a function of the rate of conversion even for complex reactions. As complex reactions will show different values of activation energy for different degrees of conversion, this method can also be used to check for conditions of first-order kinetics.

Accurate estimation of thermal endurance from kinetic experiments requires careful testing procedures and adequate mathematical algorithms. In particular, the specimen temperature shall be known with high accuracy and shall be stable for the whole test length, in case of isothermal tests. Therefore, additional tests are required varying specimen setup (e.g. mass, conditioning and preparation), and test procedures (e.g. heating rates, concentration and flow rate of purge gases) to prove that the kinetic parameter estimates are robust and really representative for the material.

4.3 Thermal endurance

Having estimated the kinetic triplet for the predominant ageing reaction, the thermal endurance characterization requires the determination of a life point, which is able to correlate the kinetic parameters, particularly activation energy, to temperature index or relative temperature index through appropriate end-points criteria. Indeed, referring to oxidation

processes, it may result in tiny fissures at the surface of the material, which will reduce the mechanical strength more than the overall conversion of the material would suppose. Hydrolysis reaction may result in an increased electrical conductivity, also more severe than the overall conversion. There is not even a simple general correlation to predict the loss of mass of conventional test specimens from thermo gravimetric data, for example because of diffusion processes.

The additional life point can be obtained therefore by conventional tests according to IEC 60216-1, IEC 60216-2, IEC 60216-5 and IEC 60216-8, with one set of samples aged at a temperature which can be as high as the one corresponding to the shortest test time according to IEC 60216-1. Typical values of mean time to end-point may be between 100 h and 2 000 h (if possible, not less than 500 h). The result of this conventional thermal endurance test will establish a correlation between degree of chemical conversion and the end-point, thus life, of the tested material. Typically, the conventional ageing evaluation of the material will be carried out at the highest temperature recommended by IEC 60216-1, for example. time to reach the end-point criteria will be between 100 h to 500 h.

Knowing the activation energy, which is proportional to the thermal endurance line slope, and the life point, HIC and TI of the candidate material can be estimated. In order, however, to avoid significant errors in the thermal endurance index estimates, due for example to the wrong choice of test temperatures in the analytical or conventional tests, or to the intrinsic lack of linearity of the life line due to variations of the prevailing thermal ageing reaction in the test and extrapolation temperature range, only a relative temperature index, RTE, can be provided. It is obtained testing the candidate and reference materials under the same conditions.

The reference materials shall not only be selected based on the expected thermal endurance which should be similar to that of the candidate material, but it shall follow a reaction mechanism very close to that of the candidate material. This requirement will be most probably fulfilled within the same group of polymers (i.e. polyolefines, epoxy resins with the same curing mechanism) designed for similar application (i.e. cables).

The reference material shall have been aged through conventional ageing test to be considered acceptable.

NOTE Degradation mechanisms seen in thermal analysis may not correspond to degradation mechanisms under end use condition because of a wide range of temperature difference between those two conditions. The correlation can be demonstrated by the reference material already having the activation energy calculated from the conventional multipoint ageing data, which verify test conditions on thermal analysis to give the material the same activation energy when it is determined by the analytical test method.

5 General basics

5.1 Reaction rate, r

For the general chemical reaction, involving reactants A,B and products P,Q:

$$aA+bB \rightarrow pP+qQ+... \quad (1)$$

occurring under constant-volume conditions, without an appreciable build-up of reaction intermediates, the reaction rate r is:

$$r = -\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{p}\frac{\mathrm{d}[P]}{\mathrm{d}t} = \frac{1}{q}\frac{\mathrm{d}[Q]}{\mathrm{d}t} \quad (2)$$

where symbols placed inside square brackets denote amount (or amount of substance) concentrations (conventionally expressed in units of mol/dm^3). The rate of reaction differs from the rate of increase of concentration of a product P by a constant factor (the reciprocal of

its coefficient in the stoichiometric equation, p) and from the rate of decrease of concentration of the reactant A by a^{-1}.

NOTE All definitions are from IUPAC "Goldbook".

5.2 Extent of reaction ξ

Quantity describing the progress of a chemical reaction equal to the number of chemical transformations, as indicated by the reaction equation on a molecular scale, divided by the Avogadro constant (it is essentially the amount of chemical transformations). The change in the extent of reaction is given by

$$\mathrm{d}\,\xi = \frac{\mathrm{d}\,n_{\mathrm{B}}}{\mathrm{d}\,\nu_{\mathrm{B}}} \tag{3}$$

where ν_{B} is the stoichiometric number of any reaction entity B (reactant or product), n_{B} is the amount of substance B and $\mathrm{d}n_{\mathrm{B}}$ is its variation.

5.3 Rate of conversion $\dot{\xi}$

The rate of conversion is defined by the quantity:

$$\mathrm{d}\,\dot{\xi} = \frac{\mathrm{d}\,\xi}{\mathrm{d}\,t} \tag{4}$$

From Equation (1) it results:

$$\dot{\xi} = -\frac{1}{a}\frac{\mathrm{d}\,n_{\mathrm{A}}}{\mathrm{d}\,t} = -\frac{1}{b}\frac{\mathrm{d}\,n_{\mathrm{B}}}{\mathrm{d}\,t} = \frac{1}{p}\frac{\mathrm{d}\,n_{\mathrm{P}}}{\mathrm{d}\,t} = \frac{1}{q}\frac{\mathrm{d}\,n_{\mathrm{Q}}}{\mathrm{d}\,t} \tag{5}$$

Where n_{A} designates the amount of substance A, conventionally expressed in units of mol. The concept of rate of conversion is appropriate when the use of concentrations is inconvenient, for example under conditions of varying volume.

In a system of constant volume, the rate of reaction is equal to the rate of conversion per unit volume throughout the reaction. For a stepwise reaction this definition of reaction rate (and extent of reaction) will apply only if there is no formation of side products. It is therefore recommended that the term reaction rate be used only in cases where it is experimentally established that these conditions apply.

5.4 Order of reaction, *n*

If the macroscopic (observed, empirical or phenomenological) reaction rate r for any reaction can be expressed by an empirical differential rate equation (or rate law) which contains a factor of the form

$$k[\mathrm{A}]^{\alpha}\,[\mathrm{B}]^{\beta}\ldots \tag{6}$$

(expressing the dependence of the reaction rate on the concentrations, [A], [B], …) where α, β are constants (independent of concentration and time) and k (reaction rate constant) is independent of [A] and [B] etc., then the reaction is said to be of order α with respect to A, of order β with respect to B, … , and of (total or overall) order $n = \alpha + \beta + \ldots$. The exponents α, β,… can be positive or negative integral or rational nonintegral numbers.

5.5 Rate law

An expression for the reaction rate of a particular reaction in terms of concentrations of chemical species:

$$r = \frac{1}{\nu_A}\frac{dc_A}{dt} = k_n {c_A}^{\alpha} {c_B}^{\beta} \quad (7)$$

Zero order reaction

$$r = k \quad (8)$$

First order reaction

$$r = k\ c_A \quad (9)$$

Second order reactions

$$r = k\ {c_A}^2 \quad (10)$$

$$r = k\ c_A c_B \quad (11)$$

6 Thermokinetic parameter estimation

The combination of the rate law for a general chemical reaction

$$r = \frac{1}{\nu_A}\frac{dc_A}{dt} = k_n {c_A}^{\alpha} {c_B}^{\beta} \quad (12)$$

and the Arrhenius equation

$$k = \exp\left(\frac{-E_a}{RT}\right) \quad (13)$$

can provide the basis for estimation of the kinetic parameters useful for the thermal endurance characterization (slope of the thermal endurance line):

$$r = \exp\left(\frac{-E_a}{RT}\right) {c_A}^{\alpha} {c_B}^{\beta} \quad (14)$$

The general principle of IEC 60216-2 to associate life with a defined end-point criterion (e.g. 5 % loss of mass, or 80 % mechanical strength) implies the use of a rate law based on the degree of conversion α, not concentration of products.

Considering that

$$r = \frac{ds}{dt} \quad (15)$$

where s is the substance undergoing conversion due to ageing reactions (correlated with the diagnostic property, p, of IEC 60216-2), the general rate law can be defined as a combination of a temperature dependent rate constant and a function describing the dependency of the reaction from the degree of conversion:

$$\frac{ds}{dt} = k(T)f(s) = A\exp\left(\frac{-E_a}{RT}\right)f(s) \tag{16}$$

For a chosen degree of conversion (s = s_L, related to the property end-point of IEC 60216-2) the activation energy could be derived as:

$$\left[\frac{\partial \ln(ds/dt)}{\partial T^{-1}}\right]_{s_L} = \frac{E_a}{R} \tag{17}$$

These definitions are the basis for all methods of “isoconversional kinetics”.

There are differential (Friedman) and several integral isoconversional methods (Ozawa–Flynn–Wall, Kissinger–Akahira–Sunose, Vyazovkin, etc.), available to calculate the activation energy and the pre-exponential factor from a set of thermograms with different heating rates and/or isothermal runs.

The function $f(s)$ holds all information about the model of the chemical reaction, completing the “kinetic triplet”. The integral form of this function is defined as $g(s)$:

$$g(s) \equiv \int_0^s \frac{ds}{f(s)} = A\int_0^t \exp\left(\frac{-E_a}{RT}\right)dt \tag{18}$$

For a single step reaction of first order and an isothermal temperature program $g(s)$ is defined by the simple equation:

$$g(s) \equiv A\exp\left(\frac{-E_a}{RT}\right)t \tag{19}$$

In this case the time to reach a defined degree of conversion s_L, that is, the time to failure or life in IEC 60216-1, can be calculated by

$$t_L = \frac{g(s)}{A\exp(-E_a/RT)} \tag{20}$$

For a first-order reaction $f(s)$ is defined by

$$f(s) = 1 - s \tag{21}$$

so that the integral form $g(s)$ is

$$g(s) = -\ln(1-s) \tag{22}$$

This allows calculating t_L for any degree of conversion ($f(s)$ and $g(s)$ are constant for a certain degree of conversion).

Replacing s with the diagnostic property p, and s_L with the end-point of p, p_L, the phenomenological approach of IEC 60216-1 is derived. Because the prevailing thermal ageing reaction is, in general, not known, the time behaviour of a diagnostic property p is measureable (see IEC 60216-2), at different temperature levels (≥ 3). The fixed end-point, p_L

(equivalent to a certain degree of conversion, s_L), failure times (that is, time to end-point or life) can be estimated at each temperature, and the thermal endurance graph can be plotted.

Accordingly, Equations (17) to (20) can be rewritten as:

$$\left(\frac{\mathrm{d}p}{\mathrm{d}t}\right) = k(T) \times f(p) \tag{23}$$

Considering, as a first approximation,

$$f(p) \approx p^s \tag{24}$$

then

$$\left(\frac{\mathrm{d}p}{\mathrm{d}p^s}\right) = k(T)t \tag{25}$$

With $p = p_L, t = t_L$ (life), thus:

$$f(p_L) = k(T) \cdot t_L \tag{26}$$

$$t_\mathrm{L} = A \exp\left(\frac{-E_\mathrm{a}}{\mathrm{R}T}\right) \tag{27}$$

where R is the gas constant and $k(T)$ the Arrhenius law (see Equation (13)). t_L is the life at test temperature T, thus one point of the thermal endurance graph in IEC 60216-1.

According to the above, for an electrical insulating material, the condition of the single point evaluation according to IEC 60216-1 can be interpreted as a special solution of the function $g(s)$. This allows estimating the temperature index from this point using activation energy from the kinetic analysis only. From Equation (20):

$$\frac{g(s)}{A} = t_1 \exp\left(\frac{-E_\mathrm{a}}{\mathrm{R}T_1}\right) = t_2 \exp\left(\frac{-E_\mathrm{a}}{\mathrm{R}T_2}\right) \tag{28}$$

so that estimation of the temperature index based on an analytical procedure, $\mathrm{RTE_A}$, can be obtained, considering t_1 = 20 000 h and $T_1 = \mathrm{RTE_A}$, and $T_2 = T_S$, $t_2 = T_{ls}$ (the temperature of the single point ageing test and relevant mean time to end-point).

$$\mathrm{RTE_A} = \left[\frac{1}{T_{LS}} + \frac{\mathrm{R}}{E_\mathrm{a}} \ln\left(\frac{t_\mathrm{TI}}{t_\mathrm{LS}}\right)\right]^{-1} - 273{,}15 \tag{29}$$

NOTE This calculation is valid strictly if the functions $g(s)$ for the analytical technique and for the ageing procedure with a different end-point criteria are identical.

7 Analytical test methods

7.1 General

Polymer compound information shall be reviewed to determine if mechanisms other than polymer decomposition (e.g. additive volatilization) are expected to affect the results from these analytical tests.

7.2 Isothermal methods

Specific methods for the experimental evaluation of the activation energy based on analytical test methods for material families will be described in other parts of IEC 60216-7. This part will provide detailed definition for pre-conditioning of materials and experimental parameters of DSC and TGA.

Isothermal procedures require an additional accelerating factor to reduce time required for testing. The most convenient method is the use of higher concentration of oxygen. For material characterization and comparison, evaluation of the isothermal oxygen induction time according to ISO 11357-6 is a well-established method.

Because of the influence of oxygen concentration on the reaction rate, an evaluation of the dependence of the reaction rate on the concentration of oxygen will also be required. Therefore OIT values at different temperatures and different concentration of oxygen are required.

If the oxidation reaction is of first order with respect to the concentration of oxygen, at least in the test and extrapolation temperature range,

$$\frac{\mathrm{d}t}{\mathrm{d}[O_2]} = const. \tag{30}$$

it is possible to combine the OIT results (activation energy) with single point thermal evaluation according to standard procedures of IEC 60216 to achieve an estimated RTE.

7.3 Model-free methods

Methods based on constant, or modulated, heating rates, without referring to a reaction model, can provide a fast access to kinetic parameter estimation without the restriction of a second accelerating factor, i.e. using air or nitrogen as purge gas.

The isoconversional models for calculating activation energy and pre-exponential factor from thermograms are quite sensitive to experimental errors and the definition of the model parameter (e.g. the required baseline function).

These methods therefore should be used with great care and additional experiments with variation of sample mass, heating rates, and sample preparation are recommended to understand the restrictions for certain material families. In particular, phase transitions of materials within the experimental temperature range may result in large errors for calculated activation energy.

Also, for the calculation process it is recommended to analyse the same data with slightly different parameters (e.g. baseline function, integration limits, calculation method) to understand the influence on the kinetic parameters.

Without an adopted reaction model and without the necessary knowledge of the restrictions of the method, results can hold large errors in RTE estimation.

7.4 Model-fitting methods

The most important degradation processes of electrical insulation materials are the thermal oxidation, pyrolysis reaction and hydrolysis. For thermal analysis with standard TGA or DSC instruments, the influence of hydrolysis is minor.

A simplified reaction model for the thermal degradation reaction can therefore be defined as 2 parallel reactions and 2 consecutive reactions which can also be auto-catalytic.

Complex kinetic models may provide better correlation of experimental data and calculated values, but this will not provide a sound proof for the reaction mechanism on a molecular level. Resilient kinetic models for specific material groups may provide a good method for the evaluation of the activation energy.

7.5 Conventional reference point

The reference point from the conventional methods shall be obtained according to the procedures of IEC 60216-8. The test temperature shall be chosen equal or lower than the highest test temperature of the conventional procedure. The higher the test temperature, the greater is the uncertainty on the estimation of TI_A and RTE_A.

8 Calculation procedures

8.1 Determination of the kinetic parameters

There are various mathematical procedures available for the determination of the kinetic parameters of the thermal degradation reaction. Most modern test equipment provides software for the calculation of activation energy from a set of thermograms (different constant temperature, heating rates or even modulated temperature programs).

NOTE 1 For an International Standard, the methods need to be defined on the basis of a round robin test.

NOTE 2 Methods accepted for certain material families will be published in additional parts of this technical specification.

8.2 Determination of analytical temperature endurance index, RTE_A, and halving interval, HIC_A

The slope of the thermal endurance line is estimated by E_a, (see Equation (17)), the location by the conventional single point test, according to IEC 60216-2. RTE_A is derived from Equation (29), while the analytical halving interval, HIC_A, is given by:

$$HIC_A \approx (273 + RTE_A)^2 \frac{R}{E_a} \log 2 \qquad (31)$$

8.3 Determination of RTE_A

8.3.1 General

The relative temperature endurance index (RTE) is a thermal endurance characteristic which is derived from the two thermal endurance relationships resulting from the comparative testing of the test material and the reference material. The RTE is specifically related to the time corresponding to the TI originally determined for the reference material.

For the determination of RTE, the thermal endurance of the chosen reference material, obtained by the conventional procedure described in IEC 60216-5 and IEC 60216-8, has to be known.

The reference material shall be of the same type as the tested material, and have a history of satisfactory service. It shall have a known temperature index, estimated by the conventional procedure described in IEC 60216-5, considering the property and end-point value which are related to its operation in service and are sensitive to the predominant ageing reaction which is investigated through the analytical procedure. The TI_r and HIC_r of the reference material should be very close to the values expected for the tested (candidate) material.

Both candidate and reference materials are tested in the same conditions and with the same analytical procedure. The conventional life test is performed at the same temperature for the two materials or at temperatures differing no more than 10 K.

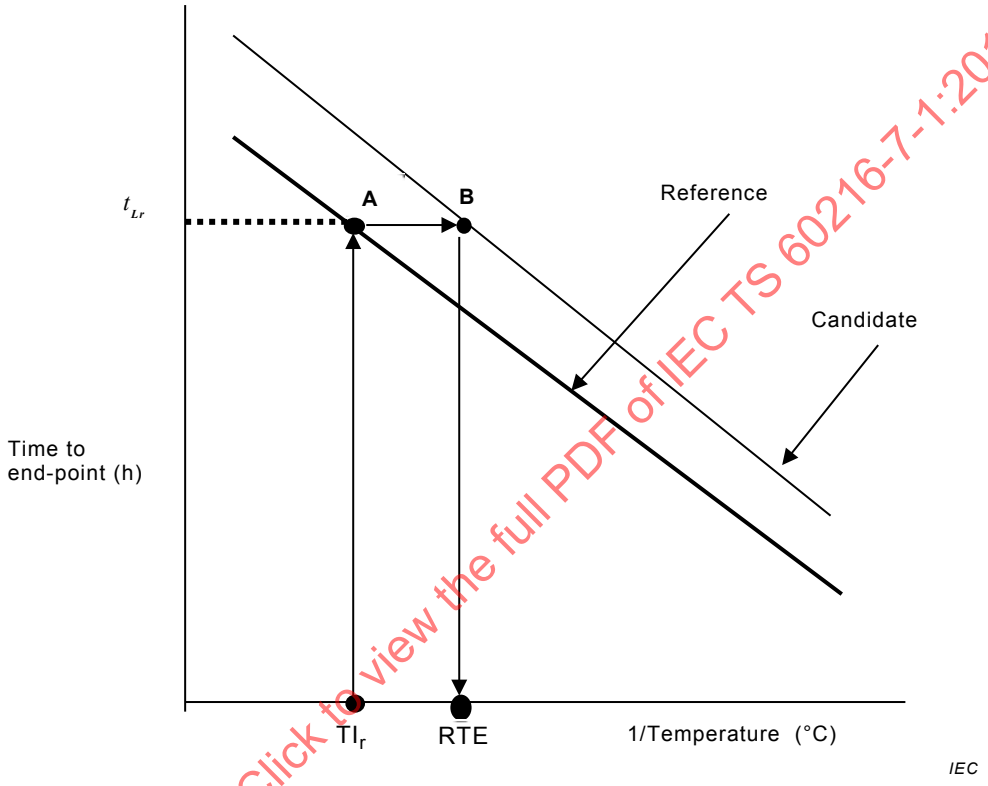

Figure 1 – Thermal endurance graph for the determination of the relative temperature endurance (RTE)

8.3.2 Calculation

The procedure is illustrated in Figure 1. TI_r is the original TI of the reference material estimated by the conventional approach described in IEC 60216-5 and t_{Lr} the mean time to the end-point of the reference material, calculated from the analytical procedure from Equation (28) where T_1 is TI_r, t_1 is the unknown t_{Lr} and $T_2 = T_{Ls}$, $t_2 = t_{Ls}$ are temperature and mean time to end-point of the single point conventional ageing test.

Determined t_{Lr}, RTE, based on an analytical procedure, RTE_A can be calculated from Equation (32):

$$RTE_A = \left[\frac{1}{T_{LS_c}} + \frac{R}{E_a} \ln\left(\frac{t_{L_r}}{t_{LS_c}} \right) \right]^{-1} - 273{,}15 \qquad (32)$$