

TECHNICAL REPORT

RAPPORT TECHNIQUE

Guidance on the interpretation of carbon dioxide and 2-furfuraldehyde as markers of paper thermal degradation in insulating mineral oil

Guide pour l'interprétation du dioxyde de carbone et du 2-furfuraldéhyde comme marqueurs de la dégradation thermique du papier dans de l'huile minérale isolante

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

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

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

**GUIDANCE ON THE INTERPRETATION OF CARBON DIOXIDE
AND 2-FURFURALDEHYDE AS MARKERS OF PAPER THERMAL
DEGRADATION IN INSULATING MINERAL OIL**

FOREWORD

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IEC TR 62874, which is a Technical Report, has been prepared by IEC technical committee 10: Fluids for electrotechnical applications.

This bilingual version (2016-01) corresponds to the English version, published in 2015-05.

The text of this Technical Report is based on the following documents:

Enquiry draft	Report on voting
10/903/DTR	10/917A/RVC

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

The French version of this Technical Report has not been voted upon.

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

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

- reconfirmed,
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INTRODUCTION

The cellulosic solid insulation of transformers and other electrical apparatus is subject to thermal degradation during their operational lifetime. This results in a progressive loss of paper's mechanical properties, such as tensile strength, which are related to the duration of the technical life of the equipment [3,4] ¹.

During its thermal degradation process (also called "ageing" in this Technical Report), cellulose forms several by-products, some of which may be detected by means of insulating oil's chemical analysis [1,2]. The concentration and rate of increase of those by-products can be used as a tool to estimate the progress of paper thermal degradation in transformers and other electrical apparatus in service.

For this reason, IEC technical committee 10 has prepared this Technical Report for the monitoring of insulating oil parameters related to cellulose ageing and the interpretation of results, as a guidance to the thermal degradation evaluation of insulating paper.

This Technical Report is based on the evaluation of cellulose ageing by-products content in insulating oil, and their rate of formation during the life of the oil-immersed electrical equipment. Statistical reference values reported in Annex A of this Technical Report are based on data collected by TC10. The final report of CIGRE WG D1.01.TF13 [7] was taken as a source of information concerning mechanisms and parameters influencing the formation of furanic compounds.

NOTE Methods for the estimation of actual degree of polymerization (DP) values of paper, which are widely available in literature, were not applied within this Technical Report. This is due to the fact that a number of different models have been developed and reported, and they often lead to different results. Moreover, the applicability of those models has not been sufficiently proven by comparison with field experience to be included into an IEC standard.

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This Technical Report does not purport to address all the safety problems associated with its use. It is the responsibility of the user of the Technical Report to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The mineral oils which are the subject of this Technical Report should be handled with due regard to personal safety and hygiene. Direct contact with eyes may cause slight irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought.

Some of the tests specified in this Technical Report involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

Environment

This Technical Report involves mineral oils, chemicals and used sample containers. The disposal of these items should be carried out in accordance with current national legislation with regard to the impact on the environment. Every precaution should be taken to prevent the release into the environment of mineral oil.

¹ Figures in square brackets refer to the Bibliography.

GUIDANCE ON THE INTERPRETATION OF CARBON DIOXIDE AND 2-FURFURALDEHYDE AS MARKERS OF PAPER THERMAL DEGRADATION IN INSULATING MINERAL OIL

1 Scope

IEC TR 62874, which is a Technical Report, provides guidance for the estimation of consumed thermal life of transformers' cellulosic insulators, through the analysis of some compound dissolved in the insulating mineral oil. A comparison between analytical results of 2-furfural (2-FAL) and carbon oxides and their correspondent typical values estimated for different families of equipment gives information on the estimated thermal degradation of papers.

The ageing rate of insulating papers can be evaluated, in short time ranges (e.g. 1 year), by regularly monitoring 2-FAL and carbon oxides content in the oil and by comparing them to typical rates of increase.

A statistical approach for the estimation of paper thermal degradation, and the evaluation of ageing rate is given.

Typical values for concentrations and rates of increase of the parameters related to paper ageing were extrapolated from a statistical database collected, and are reported in Annex A. They may be used as a rough guide, but they should not be considered as threshold values.

This Technical Report is only applicable to transformers and reactors filled with insulating mineral oils and insulated with Kraft paper. The approaches and procedures specified should be taken as a practical guidance to investigate the thermal degradation of cellulosic insulation, and not as an algorithm to calculate the actual degree of polymerization (DP) of papers.

The paper thermal life evaluation protocol described in this Technical Report applies to mineral oil impregnated transformers and reactors, insulated with Kraft paper. Any equipment filled with insulating liquids other than mineral oil (i.e. esters, silicones) or insulated with solid materials other than Kraft paper (i.e. TUP – thermally upgraded Kraft paper, synthetic polymers) is outside of the scope of this Technical Report.

This Technical Report is applicable to equipment that has been submitted to a regular monitoring practice during the service, and for which maintenance and fault history is known.

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.

None.

3 Significance

3.1 General

This Technical Report describes a statistical approach to paper thermal life evaluation. This means that all typical values are obtained from populations of transformers belonging to the same family for technical characteristics and application (see Annex A).

The approach used to collect statistical data, described in 6.1, can be applied by utilities or owners having a large population of units, to calculate individual reference values related to a specific family of transformers or reactors. This is very important because different population of transformers (i.e. operating in different climates or under different operational conditions) may have different typical values.

NOTE For an extensive survey on furanic compounds as markers for diagnosis of paper insulation degradation, see CIGRE Brochure 494/2012 [7].

3.2 Thermal and mechanical degradation of paper

3.2.1 General

There are main factors: design and materials, contaminants in the insulation system and operational conditions, that will determine the ageing of a transformer [1,2]. For the solid insulation – paper and pressboard – it means a combination of mechanical and dielectric performance, which are interlinked and synergetic. For a transformer, in the context of thermal ageing, it is the mechanical strength of the paper that matters. The ageing of paper results in a decreased mechanical strength and is assumed to reduce the ability of the transformer to withstand short circuit stress. This, however, has not been statistically demonstrated, yet.

Tensile strength, elongation and folding strength all decay with time, and more quickly at higher temperatures.

The mechanical performance of cellulosic insulation is given in terms of tensile index or degree of polymerization (DP), which are strongly influenced by ageing. The DP value is an average value of chain lengths of the cellulose molecules given as a number of glucose rings in a cellulose chain. It is measured through measurement of the viscosity of a paper solution, according to IEC 60450 [8].

It is more convenient to perform DP than tensile index, because of the limited amount of paper accessible for tests; therefore it is widely used for the evaluation of the cellulosic ageing status.

There are three main processes of degradation:

- hydrolysis;
- oxidation;
- pyrolysis.

3.2.2 Impact of temperature

Temperature affects the rate of degradation. This fact is reflected in IEC 60076-7 [3] and IEEE Std C57.91 [4] transformer loading guides.

IEC 60076-7 [3] suggests in accordance with Montsinger that the life of a transformer can be described according to Equation (1):

$$\text{Life duration} = e^{-p \times \theta} \quad (1)$$

where:

p is a constant (a value of 6 is suggested in the range 80 °C to 140 °C)

θ is the temperature in degrees Celsius.

This is a simplified version of Arrhenius law used in IEEE Std C57.91 [4].

Since a precise end-of-line criterion for a transformer is not really available, IEEE and IEC standards use an approach where ageing rate is considered. This is the inverse of lifetime – in Montsinger form:

$$\text{Rate of ageing} = \text{constant} \times e^{p \times \theta} \quad (2)$$

The constant in Equation (2) is dependent on many parameters, e.g. original quality of cellulosic products as well as environmental parameters (moisture content and oxygen in the system). A graphical representation of these influences is shown in Figure 1.

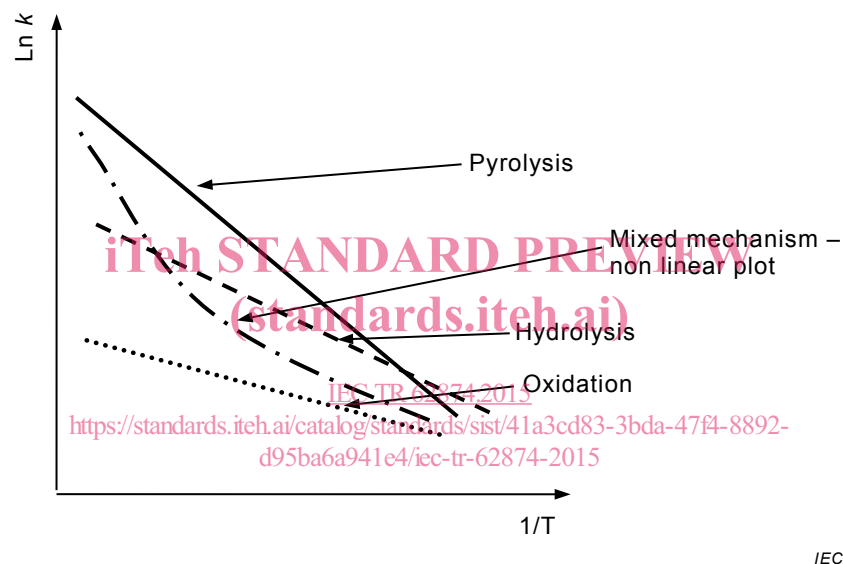


Figure 1 – Schematic diagram showing rate of ageing k , depending on different ageing mechanisms

3.2.3 Impact of humidity and oxygen

Humidity and oxygen ingress (oxidation) have an important impact on the ageing of Kraft paper. This means not only that the mechanical strength of paper rapidly decreases under ingress of moisture and air, but practically causes an increasing contamination of the combined liquid-solid insulation under these conditions. It is a consequence of the degradation products formed from oil and paper leading to a further degradation.

During the ageing of the combined cellulosic and oil insulation many by-products are formed – carbon oxides, water, acids, sludge and furanic compounds. Many of these degradation products, e.g. furanic compounds, are soluble in oil and stable enough to be used as diagnostic markers. Furanics are formed by dehydration reactions following hydrolysis of the cellulose and hemicellulose as well as by oxidative pyrolysis of cellulose. Their analytical determination is well known and reliable (see IEC 61198 [12]).

In a transformer all these processes – hydrolysis, oxidation and pyrolysis – act simultaneously, resulting in a non-linear mechanism (see Figure 1). Which process will dominate depends on the temperature and the operational parameters. In fact the application of one activation energy, although often practiced, is very difficult because of the complexity of the degradation processes.

3.3 Symptoms of paper ageing in insulating oil

3.3.1 General

The ageing of paper can be detected by direct investigation on the paper or by the measurement of by-products dissolved in the oil.

Cellulose degradation mainly affects the mechanical properties (tensile strength, elongation, burst strength, double fold strength, etc.) of paper (see Figure 2), but a direct measure of those parameters requires the sampling of a large amount of paper, which is normally impossible during the operational lifetime of a transformer. However, the relationship between the mechanical indexes and the degree of polymerization (DP) is well known. Degradation of paper does not significantly affect its resistance to the compression forces mostly and continuously applied to transformer windings through clamping.

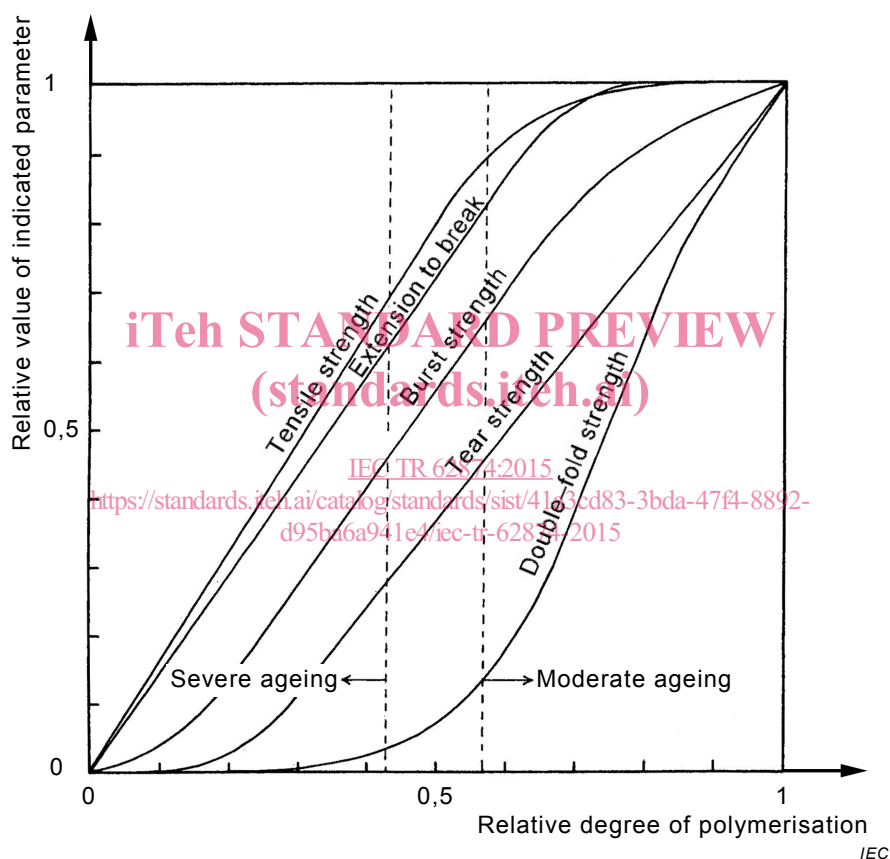


Figure 2 – Relationship between mechanical properties of insulating paper and paper degree of polymerization (DP) [5]

The DP value is the average number of glycoside rings in the cellulose polymer; in the native cellulose DP may be as high as or more than 10 000 units but after the purification process and other treatments the DP value of the electrical Kraft paper decreases to around 1 000 units (typical value: 1 200).

DP is measured in accordance with IEC 60450 [8], through measurement of the specific viscosity of a very small amount of paper dissolved in cupri-ethylene-diamine (CuED). From this measurement the intrinsic viscosity of solution is deduced and from this, using the Martin's formula, the DP value is easily calculated.

By-products of aged paper may be classified as volatile, soluble and insoluble, and are dependent on the specific decomposition process: pyrolysis, hydrolysis or oxidation.

3.3.2 Volatile by-products

Carbon oxides (CO and CO₂) are the ultimate products of cellulose degradation and are measured with dissolved gas analysis (DGA) in accordance with IEC 60567 [9]. It must be taken into account that both CO and CO₂ can be generated from oil oxidation as well.

Water can reach several per cent of the paper weight. Most of the water formed is adsorbed and retained in the solid insulation of the transformer and only a little part is dissolved in oil. Of course another contribution to total water is the ingress of moisture from atmosphere.

The detection of water in oil is performed in accordance with IEC 60814 [10].

3.3.3 Soluble by-products

A large number of oil soluble compounds (acids, alcohols, etc.) are generated from paper degradation. The most commonly used compound for diagnosis is 2-furfural (2-FAL) and its related compounds:

- 5 hydroxymethyl 2-furfural (5-HMF)
- 2 furfuryl alcohol (2-FOL)
- 2 acetylfuran (2-ACF)
- 5 methyl 2-furfural (5-MEF).

The detection of 2-FAL and related compounds in oil is performed in accordance with IEC 61198 [12].

In the same way as with water, a relevant amount of generated furanic compounds is retained in the bulk of the paper. The ratio between the concentration of furanic compounds in the paper and in the oil differs for each single compound, and is affected by temperature. Increased temperature forces the equilibrium of furanic compounds to a higher concentration in the oil. Decreased temperature forces the equilibrium of furanic compounds to a higher concentration in the paper, especially in the case of dry paper.

Paper humidity and type of paper also influence the oil-to-paper concentration ratio of furanic compounds. A wet paper tends to retain a larger amount of furanic compounds, thus reducing the oil-to-paper concentration ratio.

Furanic compounds are not highly stable, and may be degraded by oxidation, mostly in oils with high oxygen content. Decay in the concentration of 2-FAL was observed in transformers during their operation, due to its inherent instability.

Acid compounds may be formed either by cellulose and/or oil oxidation, and a high acidity often accompanies other symptoms of paper ageing.

3.3.4 Insoluble by-products

Severe paper ageing can finally lead to the fragmentation of polymeric cellulose, and small paper fibres can be detached from the paper mass.

The cellulose fibres can be detected as particles present in insulating oil, in accordance with IEC 60970 [11].

3.4 Operational parameters influencing paper thermal ageing

In addition to transformer hours of service as a key parameter in defining “real age” of paper insulation in normal working regimes, other operational parameters such as load, type of cooling and transformer sub-type have a major influence on paper thermal ageing. The nature of the oil may also be a fundamental parameter for the estimation of paper thermal ageing.

The high-load of a transformer, implying elevated operating temperatures, promotes the paper thermal degradation process, observed with some types of transformers that are often overloaded (shunt reactors, HVDC, generator step-up (GSU) in thermal power plants (TPP), high voltage inter-tie transmission transformers).

The type of cooling, in terms of cooling media (water or air) and type of flow applied (forced or natural convection), affects efficiency of heat removal, thus influencing the rate of paper thermal degradation. The most efficient cooling can be achieved by applying water as coolant in forced oil flow.

For example, it was observed in most cases that the degree of paper degradation with GSU transformers in hydro power plants (HPP) is lower than with thermal power plant GSU units, having a similar service duration. These findings are correlated to different types of cooling (OFWF versus ONAF and OFAF), hours of service and loading history of HPP and TPP units [6].

Among different transformer sub-types, air-breathing transformers are subjected to more intensive paper degradation than sealed ones, due to higher oxygen and moisture content. Elevated concentrations of oxygen and water accelerate the paper degradation process.

Since the paper degradation process is temperature driven, every environmental and operational condition that may affect the temperature can also modify the degradation rate of the solid insulation. An elevated environmental temperature or a high loading can thus increase the rate of paper degradation, resulting in a sudden increase of 2-FAL, CO₂, CO and other by-products.

3.5 Role of oil type and condition

Oil type may affect the ageing rate of paper. Inhibited oils show a lower tendency to form acidity, and the oxidation process is slackened; the effect of oxygen in the paper oxidation process is reduced.

Transformers impregnated with inhibited oil may show a lower content of 2-FAL if compared with units insulated with an uninhibited oil, even if showing the same degree of polymerization (DP) of the paper.

The effect of passivators (triazole derivates) in the ageing of celluloses is still not well defined. By definition, metal passivators may induce a lower rate of the oil degradation process by deactivating the copper catalyst in oxidation processes, therefore slowing down the paper degradation process, but influence of metal passivators on 2-FAL concentration in the oil may not be straightforward. Some laboratory studies have shown that papers impregnated with oils to which a passivator has been added, may have a lower tendency to form furanic compounds; this may lead to optimistic estimation of ageing in presence of triazolic passivators.

The ageing condition of the oil may also affect the partition of furanic compounds between solid and liquid insulation; acidic oils may result in an increased 2-FAL concentration in oil, due to its augmented capability to extract polar compounds from the paper.

3.6 Fault conditions that may affect thermal ageing

In transformers where the degradation mechanism may be either thermal or electrical, the rate of paper degradation may increase rapidly as a consequence of significant temperature rise. High energy thermal and electrical faults involving excessive currents circulating through the insulation and large current follow-through lead to extensive destruction and carbonization of paper.

In presence of local thermal degradation due to a fault, the estimation of the paper's consumed thermal life may become very difficult, since the extension of the paper volume

involved is unknown, and temperature may have strong variations even over a short time. Investigations on the presence of thermal faults through DGA should always accompany thermal life evaluation, to avoid misleading conclusions.

High energy electrical faults (discharges of high energy) usually involve a very small volume of paper, so that the contribution to the detected concentration of furanic compounds is negligible. In case of discharges with paper involved, a sharp increase of carbon oxides is observed, rather than an noticeable increase of 2-FAL. The formation of cellulose by-product has not been found to be related to partial discharges.

3.7 Maintenance operations that may affect thermal ageing indicators

3.7.1 General

Maintenance operations on the oil may affect (partially or totally) parameters used as indicators of cellulose thermal ageing (see 3.3). Their effects should be taken into account during the estimation of the total 2-FAL concentration, and in evaluating the rate of increase of the thermal ageing indicators.

3.7.2 Effects of oil reconditioning

Oil reconditioning may reduce 2-FAL concentration in oil, depending on the duration/efficiency of the treatment.

Oil reconditioning normally does not significantly affect 2-FAL gas and moisture concentration in cellulose. On-line degassing or long-term reconditioning may reduce moisture in paper.

The equilibrium of 2-FAL distribution between oil and paper is restored in a time depending on temperature, cooling and oil circulation.

Dissolved gases and water dissolved in oil are mostly removed by vacuum degassing.

In the 6 months following a reconditioning, the rates of increase of 2-FAL, dissolved gases and moisture should not be considered as an indicator of increased ageing rate, the equilibrium being forced thermodynamically through the increase of concentration in the oil.

3.7.3 Effects of oil reclamation

Reclaiming the oil has major effects on the concentration of 2-FAL. Furanic compounds are polar and they are almost completely removed by fuller's earth and other adsorbing media.

After an oil reclamation the trend of furanic compounds should be carefully recorded (with frequent sampling) to monitor the increase of 2-FAL, taking into account new equilibrium conditions.

NOTE For effects of reclamation on dissolved gases and moisture see 3.7.2

3.7.4 Effects of oil change

Oil change has major effects on the concentration of 2-FAL, as well. All the by-products dissolved in the oil are removed. Nevertheless, after an oil change a new equilibrium between solid and liquid insulation is dependent on temperature, cooling and oil circulation.

After an oil replacement the trend of furanic compounds should be carefully recorded (with frequent sampling) to monitor the increase of 2-FAL, taking into account new equilibrium conditions.

NOTE For effects of oil change on dissolved gases and moisture see 3.7.2