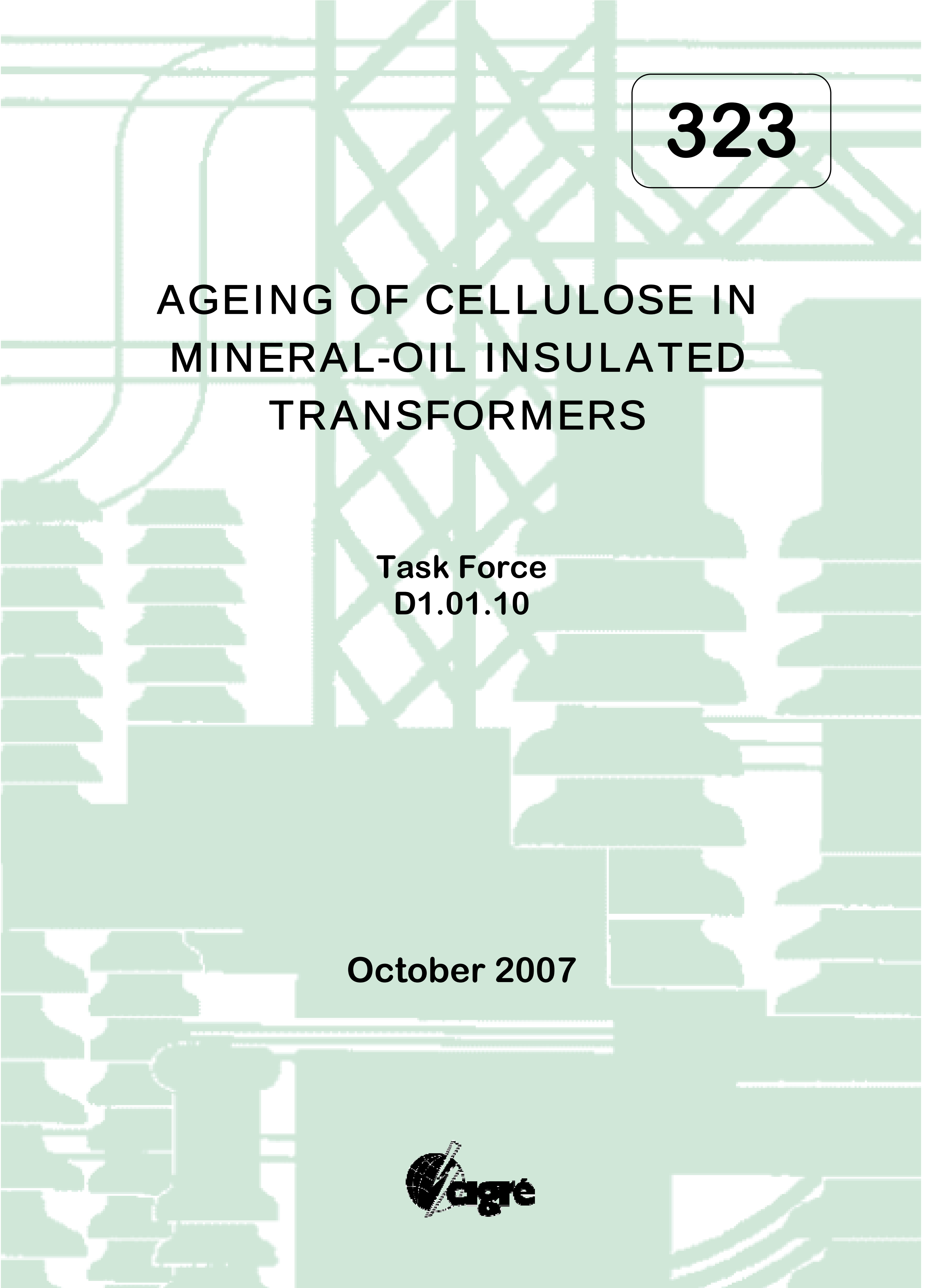

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AGEING OF CELLULOSE IN MINERAL-OIL INSULATED TRANSFORMERS

Task Force
D1.01.10

October 2007

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n° ISBN : 978-2-85873-018-6

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1 EXECUTIVE SUMMARY

1.1 BACKGROUND

Ageing of power transformers is a growing concern of utilities around the world as power systems grow older and demands on power quality become ever more important. Oil-cellulose transformer insulation will irreversibly age, and the cellulose insulation cannot be renewed. The question of transformer ageing and renewal is further accentuated by power grids and stations operating at increased loads, higher potential overloading and larger and more frequent load changes. The loading guides describe how loss of life is influenced by time and temperature.

The ageing of the oil-impregnated cellulose insulation and the associated loss of mechanical strength is one of the important factors that limit the life expectancy of a transformer. It is commonly acknowledged that the ageing is governed by temperature. Transformers, using cellulose insulation, are normally assumed to operate for decades at nominal load at a specified ambient temperature. Research shows that contaminants like water, acids and oxygen influence the ageing of solid and liquid insulation significantly. The role of these contaminants is not considered in the loading guides.

From a utility perspective the important questions are:

- What are the ageing mechanisms?
- How do temperature, water, dissolved by-products etc. act on insulation ageing?
- Which diagnostic indicators can be used to assess ageing?
- How can ageing be slowed down?
- Which maintenance practices can be recommended to extend transformer life?

TF D1.01.10 was established to report on the normal ageing of cellulose; i.e. at design temperatures for continuous service and accepted overloads. Different practices concerning transformer materials and design (e.g. sealing) have to be considered. Important issues discussed are how ageing proceeds depending on the transformer materials, transformer condition and service conditions etc. Furthermore, what are the possibilities for diagnosis, life assessment and maintenance? The report examines additional aspects of material ageing (i.e. role of oxygen, water and acids) not reflected in the loading guides.

1.2 MAJOR FAILURE SCENARIO

For cellulose insulation, the important issue is how ageing influences the mechanical rigidity of a winding; the major failure scenario being winding movement resulting from high mechanical stresses during short circuit. What is important is the rigidity of the paper, its ability to withstand shear stresses between conductors and spacers, and the changing of the winding compression resulting from changes in the shape and elasticity from plastic deformation of paper and pressboard.

1.3 MATERIALS

In power transformers, cellulose is used in various forms as a solid insulation material. Insulation made from pure "kraft" pulp provides outstanding oil impregnation characteristics and thus excellent performance in electrical fields. Cellulose materials also have good geometric stability in oil, are easy to mould, wrap, bend, saw, grind, mill (depending on thickness) and are still by far the most economic solid insulation for oil cooled power transformers.

For the manufacturing of paper and pressboard for electrical insulation, mainly unbleached softwood kraft pulp is used. The cellulose is refined from the tree by the so-called "sulphate" or "kraft" process. After processing the typical composition of unbleached kraft pulp is 78-80% cellulose, 10-20 % hemicellulose and 2-6 % lignin.

Cellulose is a linear condensation polymer consisting of anhydroglucose joined together by glycosidic bonds, Figure 1. The degree of polymerization (DP) - being the average number (n) of glycosidic rings in a cellulose macromolecule - is in the order of 1200 for unbleached soft wood kraft.

From kraft pulp various types of paper and pressboard having varying density are made. By adding various nitrogen containing compounds the ageing characteristics of the cellulose may be improved. With normal kraft paper the design maximum hotspot temperature inside the top of windings is 98 °C, while with thermally upgraded paper the equivalent hotspot design temperature is 110 °C.

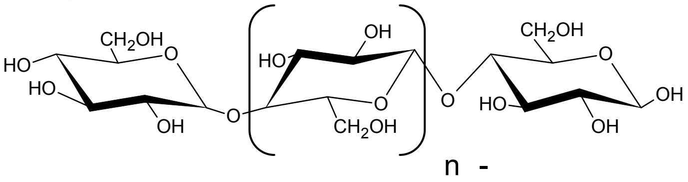

Figure 1: Structural formula of cellulose.

1.4 AGEING OF CELLULOSE

IEC’s loading guide suggests in accordance with Montsinger, that the ageing of transformer insulation is doubled (or halved) for every 6 °C in the range 80 -140 °C. This is a simplified version of the Arrhenius law used in IEEE’s loading guide. It is the mechanical strength (usually tensile strength) of the paper that is essential and a reduction down to 50 % is considered as a value indicating the end of life. Measurement of DP value of paper has become more frequently used than mechanical strength. It is a simpler tool for assessing samples taken from older transformers. Figure 2 shows a typical correlation between tensile strength and DP value. However, as it is practically impossible to take samples from the critical hot-spot region one is left to making intelligent estimates based on ageing models.

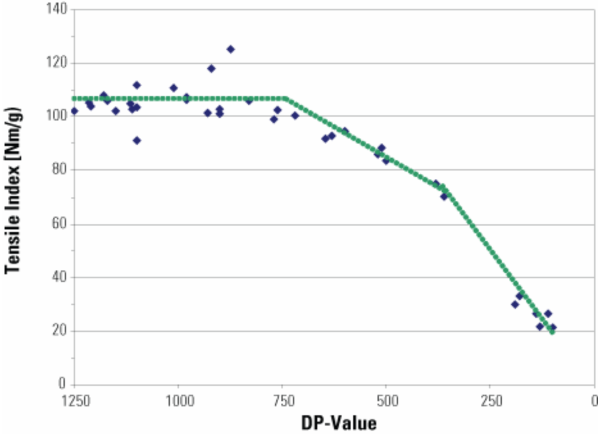

Figure 2: Correlation between tensile strength and DP value for kraft paper.

The DP value of the cellulose is reduced from its starting value (DP_0) due to molecular cellulose chains being cut. The relation between the chain scissions (η) and measured DP_t is:

$$\eta = \frac{DP_0}{DP_t} - 1 \qquad (1)$$

The ageing of paper is often described by the following Arrhenius relation:

$$\frac{1}{DP_t} - \frac{1}{DP_0} = A \cdot e^{\frac{-E_A}{RT}} \cdot t \qquad (2)$$

Here, R is the molar gas constant (8,314 J/mole/K), T the absolute temperature in Kelvin and E_A is the *activation energy* in kilojoule per mole. The pre-exponent value A is a constant depending on the chemical environment.

It is now commonly accepted that cellulose ageing may be described by the following processes:

- Hydrolysis, which is a catalytically governed process where the rate of chain scissions depends on carboxylic acids dissociated in water. As both water and carboxylic acids are produced during ageing of cellulose this process is auto accelerating.
- Oxidation, suggested to be catalyzed by hydroxyl radicals (HO•), which are produced by decomposition of hydrogen peroxide, H_2O_2 and of organic hydroperoxides (ROOH).
- Pyrolysis which can take place without access to water and/or oxygen, or any other agent to initiate the decomposition. At normal operating or overload temperatures (i.e. <140^{o}C) pyrolysis is of little relevance.

In a real transformer all these processes – hydrolysis, oxidation and pyrolysis act simultaneously, resulting in a non-linear Arrhenius plot. This hampers the application of one model describing the full complexity of the degradation processes. Which process will dominate depends on the temperature and the condition (i.e. oxygen, water and acid content). Furthermore, it is important to realize that different degradation processes in real life do not act independently of each other. The ageing rates' dependence on temperature (i.e. activation energy) will vary depending on the process dominating in the specific temperature region as suggested in Figure 3. It looks like the ageing by oxidation is less temperature dependent than hydrolysis and while hydrolysis doubles for every 6-7 ^{o}C, oxidation needs a temperature increase of 8-9 ^{o}C to double.

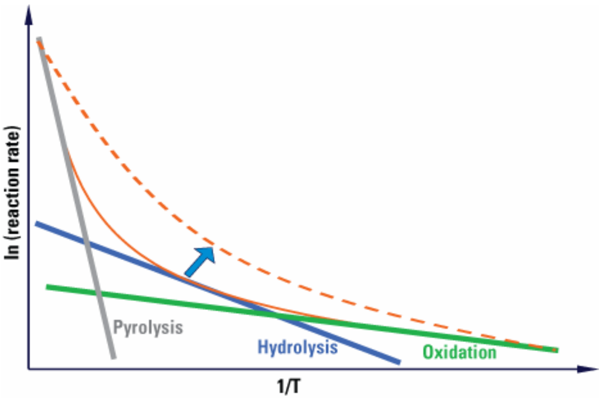

Figure 3: Arrhenius plot of ageing rates due to different ageing mechanisms. The arrow shows the effect of increased water content on the preexponent A-value for hydrolysis. X-axis is inverse temperature

The condition of the insulation system is important for which ageing mechanism that will be dominating. For kraft paper it seems from lab experiments that the degradation rate is close to being proportional to the water content, while the effect of oxygen is less pronounced. The difference in ageing rate between an almost oxygen-free environment and air-saturated oil appears to be in the region of 2 to 3. It appears that low molecular weight water soluble acids play a significant role in the hydrolysis, but further work is needed to shed more light on this. In addition some thermal upgrading systems seem to have a significant effect, at least at hydrolysis.

1.5 INTERACTION WITH OTHER AGEING PROCESSES

Cellulose is not the only material that ages: the oil will also age, predominantly from oxidation, forming various carboxylic acids, some of which may contribute to the paper ageing. Peroxides formed during interaction with active metals are another source of synergetic effects. Furthermore, sludge may form from oil ageing and this sludge may, when deposited on the paper, reduce the cooling of the winding and therefore lead to increased ageing of the cellulose by increasing the temperature.

1.6 DIAGNOSTICS

Water

Water is produced by ageing and is also an important ageing accelerator that significantly influences the ageing rate. In order to assess the ageing rate it is therefore important to measure the water content of the cellulose correctly. It is now clear that the indirect scheme using equilibrium curves for assessing moisture in paper via measured water content in oil can give significant errors, due to changes in the water solubility for aged oils. Errors of a factor of two are possible. It appears that this is mainly due to an increased content of low molecular weight acids in the oil that increases the water solubility, thereby changing the partitioning of water between oil and cellulose. Nevertheless, in spite of its shortcomings, this indirect method still has its use. CIGRE WG A2.30 is presently reporting on moisture dynamics of transformers.

Furanic compound analysis

Furanic compounds are a group of chemicals formed both by oxidation and hydrolysis of cellulose. A lot of faith has been put in these as chemical markers for assessing the ageing state of the cellulose. However it is now apparent that temperature dependent partitioning between oil and cellulose has to be considered, as have moisture, acidity, stability etc. Also one has to consider that production of furanic compounds will depend on the degree of ageing - being distributed through the winding - and the amount of materials involved. Finally, it appears that thermally upgraded cellulose does not produce furanic compounds to the same extent that normal kraft paper does. This has all led to a more reluctant attitude towards accepting simple relations between furanic compound concentrations and winding ageing. CIGRE TF D1.01.13 pursues this complex issue.

Dissolved gas analysis

Water and carbon oxides are the main by-products from cellulose degradation. However, other degradation processes produce these gases and they may come from the outside atmosphere. Since the cellulose material is the main producer of carbon oxides these gases can be used for a rough assessment of the cellulose ageing. This assessment is based on gas levels, production rates and on ratios. Recently CIGRE joint task force JTF D1-01/A2-11 made an extensive summary of typical absolute values and gas increase rates.

Other markers

Presently work goes on with gas chromatography and HPLC techniques to identify other oil soluble markers suited for diagnostics and many interesting substances are identified (e.g. carbohydrates, alcohols and acids). More work is indeed necessary on the low molecular weight acids, also due to their participation in hydrolytic ageing.

Dielectric diagnosis

Dielectric response methods (FDS, PDC and RVM) are promoted for measuring water in cellulose as explained by CIGRE TF D1.01.09. It appears that ageing by-products like carboxylic acids may act somewhat like water in these measurements. However, the effect on the dielectric response from ageing seems small compared to that of water, and dielectric methods can therefore not be expected to offer an alternative to chemical diagnostics.

1.7 MAINTENANCE ASPECTS

The chemical degradation of the cellulose can, as explained above, be described with some confidence by Equation 2, which can be rearranged for life assessment:

$$Expected\ Life = \frac{\frac{1}{DP_t} - \frac{1}{DP_0}}{A \cdot 24 \cdot 365} \cdot e^{\frac{E_A}{RT}} \ [year] \qquad (3)$$

DP_0 is in the range 1000 - 1250 for a new transformer. DP_t is defined by the user from his preferred margin of safety for the transformer, but frequently a DP value of 200 is used as an end of life criterion. Paper is then very brittle and cannot withstand folding. We see that life is inversely proportional to the pre-exponent *A* value, which is governed by contamination of the insulation system as explained above.

From a maintenance perspective the important questions are:

- How can ageing accelerating substances in the materials of the transformer be avoided in new units?
- How can one avoid occurrence of ageing accelerating substances in the transformer during service?
- How can ageing accelerating substances be removed from a transformer and when is such refurbishment a profitable project?

The basis for a long transformer life is good design, and good materials which are adequately dried. One may keep contamination low by moisture absorbers, vacuum pumps and sealing membranes. To some extent oil maintenance will have a positive effect on the cellulose insulation as well, but if a transformer has ended up with a significant contamination, more efficient techniques are needed.

The possibility of removing any substance from the cellulose will depend on the extraction efficiency in the surroundings of the cellulose (oil, air or vacuum). This will mainly be governed by partitioning of the contaminant between cellulose and oil, the vapour pressure of the contaminant and chemical bonding between contaminants and cellulose. The partitioning of water is fairly well understood and techniques for removing water from the solid insulation are described extensively in Cigré Brochure No 227. However as acids of low molecular are not treated specifically it is useful to give them some attention here. These acids will, like water, stick to the cellulose. There seems to be a synergetic dependence between solubility of water and low molecular weight acids in the oil. While the lowest molecular weight acids have a boiling point close to that of water, the boiling temperature increases with the molecular weight.

Relevant techniques for refurbishing cellulose insulation are: (1) Vapour phase techniques, (2) Hot oil spray (which also can be combined with low frequency heating), (3) Hot air circulation and vacuum extraction, and (4) Liquid circulation with extraction. One should be aware that clamping pressure increases with moisture and that drying may lead to a reduction even below the initial pressure when the transformer was new and dry.

1.8 TEST TECHNIQUES FOR MATERIAL AGEING PERFORMANCE

Standardized tests can be found in the referenced national and international standards. They may be of direct or indirect interest for power transformers. Care should be taken that any accelerated test replicates service conditions. For example: liquids with increased water solubility may at high temperature dry out cellulose to an unrealistic level compared to service conditions where in almost all cases most of the water will remain in the cellulose - thereby reducing hydrolysis and leading to wrong conclusions.

2 INTRODUCTION

2.1 BACKGROUND AND AIM OF WORK

This report discusses the ageing of cellulosic insulation materials in mineral oil impregnated insulation systems for transformers and reactors. The focus will mainly be on critical paper at the windings hot spot, but will also cover cellulose in general as it will age in similar ways and produce markers that must be considered in a diagnostic evaluation.

In most countries the age of the transformer populations spans a long period with average age in the 30 year range; the oldest ones being installed in the 1940s and 1950s. It is well known that the transformer insulation system ages. As the transformers - when acquired - were designed for a 30 years lifetime, one can understand that owners are concerned when to replace them and how risk increases with age. However, experience tells that transformers may remain in service for 50-60 years without failures, and that owners may be able to postpone reinvestments. The question of transformer ageing and renewal is further accentuated with the operation of power grids and stations moving towards increased loads, higher potential overloading and larger and more frequent load changes.

For correct functioning, each transformer winding needs to be insulated turn from turn and from coil to coil. Several solid insulating materials can be used for this purpose. In power transformers, cellulosic insulating paper, also known as kraft paper, is by far the most widely used material, although nowadays other synthetic insulating materials are used to insulate the areas where the operating temperature is believed to be high (hybrid insulation), or for entire transformers specially designed to operate at high temperatures. These materials (e.g. aramide papers) should be considered very special cases, and their behaviour will not be considered in this document (for more information on these materials and their applications, see document IEC 60076-14/TS).

In a recent CIGRÉ study [1] utilities requested more information about paper/oil ageing on:
- Which diagnostic indicators are correlated with ageing?
- What are the ageing mechanisms?
- Which parameters like temperature, water, dissolved by-products act on insulation ageing?
- How to slow insulation ageing rate?
- Which maintenance practices could be recommended to extend transformers life?

Regarding ageing of cellulose insulation, the most important issue is how this ageing influences the mechanical rigidity of a winding: the major failure scenario being winding movement resulting from high mechanical stresses occurring during short circuit and possibly during multiple inrush currents. It is the rigidity of the paper; its ability to withstand shear stresses between conductors and spacers, and the changing of the winding compression; the possibility for changes in the shape and elasticity from plastic deformation of paper and pressboard again, which are important. We will mainly cover the first of these, but give some information about the others.

As the transformer ages the mechanical strength (e.g. tensile strength) of the paper will be reduced. This comes about because the fibers of the cellulose are weakened due to chemical reactions cleaving the long chains of the cellulose molecules. We will cover these reactions in detail, since they are important for understanding the rate of the ageing and because many of these chemical processes produces markers that have a potential for diagnoses of the state of the solid insulation.

Ageing accelerates with temperature from what we will call normal temperatures to direct failure conditions from e.g. bad soldering or clogged cooling channels. During failure condition the temperature may reach several hundred degrees centigrade. We are here only concerned about normal ageing (i.e. ageing as occurring before thermal failures).With normal operation we understand the temperatures the transformers are designed for during continuous nameplate load and accepted overloads. The temperatures considered here would be below about 150°C. These conditions are described in the standards (e.g. IEC 60076-7). The IEC loading guide describes how loss of life is influenced by time and temperature. One element lacking here is consideration of the condition of the insulation system; the content of water, oxygen, other ageing accelerators, oil quality etc. Most likely the same chemical reactions do not occur during normal modes (most often being below 90°C) and failure modes, and extrapolation from one condition to the other must be avoided.

There are a number of possible and related ageing effects that are relevant and should be considered in a risk assessment, which are not covered in this work. We mention here but a few of these. Several studies have confirmed that even if the cellulose system ages and the mechanical strength is reduced, the withstand voltages of the insulation is little affected [2]. We are here not concerned about effects ageing has on withstand voltages. Over time the transformer will age and its condition change: water content increases due to water ingress and formation. Moist cellulose fibers in the insulation system may initiate breakdown streamers [3] and also reduce breakdown voltages [4]. Water content in cellulose will also reduce the PD-inception voltage [5]. If water content becomes very high locally it may result in dielectric losses and formation of blisters in pressboard. With time cellulose fibers may together with sludge clog oil channels and reduce cooling of the winding. Finally, there has been a concern on copper sulfide lately, as several transformers have failed due a formation and growth of this conductive substance within and on the paper. For the time being this is considered to originate mainly from oil and copper. However, the presence of paper may influence the process.

2.2 PAPER AGEING AND TRANSFORMER RISK ASSESSMENT

Reduced strength of paper from normal ageing may be a direct or indirect cause of a failure. Future progress of cellulose ageing and the risks following this requires preparedness from utilities and service providers. It is in this context we must see this work.

What we mainly discuss here is the ageing of paper; mainly as studied in a series of laboratory experiments. The scatter in experimental results is significant. Furthermore, even if the conditions in these experiments well simulate the condition in a real transformer, the real situation is always more complex: temperature and water content varies along the winding, there are several different qualities of paper (eg. thermally upgraded or normal Kraft paper), and the paper is present in many layers with temperature and water content gradients. Also cellulosic materials like pressboard and wood are used. Simple formulas may give insight in ageing mechanisms, but are never sufficient for assessing the condition of a whole winding. Having said that we still believe that one should base the analysis on the weakest link consideration, where it will be the conditions around the hotspot region in the transformer that are the most critical. Ageing will be most pronounced in this region within the top end of the winding, and electro-mechanical forces will be strong here. If the tensile strength in this region is insufficient to withstand these forces, this will be the most likely place for a failure to occur.

Furthermore, even if we have an end-of-life criterion for the strength of the paper or the degree of polymerization of the cellulose, there is the always question of how strong the stresses are. The possibility of a failure is different for transformers, which are placed in grids where the transformer rarely experiences a short circuit or where the short-circuit currents are lower than what the transformer is dimensioned for, than for transformers exposed to frequent and high short circuit stresses from e.g. line to ground failures on power lines due to lightning, or when moved from one place to another.

Finally, in asset management an engineer will not only look at failure probability, but also on failure consequences to get the correct picture of the risk involved with a certain specific transformer or a larger fleet of transformers.

2.3 REINVESTMENTS, MAINTENANCE AND CONDITION CONTROL

Analyses of the ageing of a transformer involves two major aspects: on one hand to decide to take actions to extend the life of the transformer and on the other hand to decide when to scrap a transformer. Knowledge of the general behavior of an impregnated insulation system and its ageing is the key to understanding the possibilities for improving service conditions for the cellulose (e.g. water content, oxygen and acid content) to slow down the ageing rate of the cellulose. There exist guides for the oil maintenance [6,7]. This report will discuss how effective different maintenance techniques may be for refurbishment and life extension of the cellulose in a transformer.

Operating conditions vary throughout the world: In Europe transformers are predominantly free breathing, while in e.g. USA and Japan they are sealed from the environment using rubber diaphragms or nitrogen cushions. This will influence the environmental conditions for the cellulose. Sealing is sometimes introduced as a retrofit, and should as such also be evaluated as a maintenance or refurbishment action.

The analysis of the answers from a questionnaire concerning maintenance practices [1] showed the main following tendencies:

- Transformers are used in production, transmission and distribution applications with an average age about 30-40 years.
- Maintenance is important: the main trend is towards condition based maintenance (CBM) and the needs tend to increase maintenance with age with a peak towards the middle of transformers life. The main triggers are conditions assessment and DGA monitoring from oil sampling.
- Utilities are trying to apply life extension of insulation by using any of the following maintenance methods :
  - Removal of water and ageing products: vacuum degassing, oil filtering and heat/vacuum drying, oil reclaiming.
  - Maintaining low oxygen content.
  - Reducing the temperature by modifying the cooling.
  - Providing better protection against external stresses.

2.4 IEC, IEEE AND CIGRE PUBLICATIONS RELATED TO OVERALL SITUATION

IEC 60422 – Supervision and maintenance guide for mineral insulating oils in electrical equipment
IEEE C57.106-1991 Guide for Acceptance and Maintenance of Insulating Oil in Equipment
IEC 60076-7 - Loading Guide for oil-immersed power transformers
CIGRE Brochure 248 – Guide on economics of transformer management

3 MATERIALS

3.1 INTRODUCTION

In power transformers, cellulose is used in various forms as a solid insulation material. Insulation made from pure "kraft"[1] cellulose provides outstanding oil impregnation characteristics, thus excellent performance in electrical fields, has good geometric stability in oil, is easy to mould, wrap, bend, saw, grind, mill – depending on thickness – and is (still) by far the most economic solid insulation for oil cooled power transformers.

Nowadays other, synthetic insulating materials are used to insulate areas where the operating temperature is designed to be high (hybrid insulation), or for entire transformers specially designed to operate at high temperatures. Such materials, for example aramid paper, are considered very special cases, and their behaviour will not be discussed in this document. For more information on these materials and their applications see IEC 60076-14.

3.2 COMPOSITION OF CELLULOSE

3.2.1 Source

Cellulose is the most important constituent of most plants. It is never found pure in nature. The cotton fibre with a cellulose content of more than 95 % is probably the purest natural source. Most commonly, in wood, plant stalks, leaves and the like, cellulose is associated with other substances such as lignin and so-called hemicelluloses, both in considerable quantities. Thus, according to the species, wood contains on a dry weight basis 40 to 55 % cellulose, 15 to 35 % lignin, and 25 to 40 % hemicelluloses. The most common sources of cellulose for industrial use are wood pulp and cotton lint. In the paper industry, cotton fibres and cotton linters are only used for very specific applications. The bulk of the cellulose pulp is made from wood.

As raw material for the manufacturing of paper pulp, either soft wood (spruce, pine, fir, etc.) or hard woods (birch, beech, maple, eucalyptus, etc.) are being used. The advantage of soft wood is its longer fibres. The typical fibre length of spruce is 2.5 to 4.5 mm whereas the typical fibre length of beech is in the range of 0.7 to 1.7 mm. For paper and board with a high mechanical strength, softwoods that grow in regions with low average temperatures (Scandinavia, Canada, Chile) are optimum.

3.2.2 Processing/Treatment

For the manufacturing of paper and pressboard for electrical insulation, mainly unbleached softwood kraft pulp is used. The cellulose is refined from the tree by the so-called "sulphate" of "kraft" process.

The trees are supplied to the pulp factory as 1 to 4 m long logs. The logs are debarked and cut into chips with a side length of 20 to 40 mm and a thickness of 5 to 10 mm, which can be stored up to 6 months. The chips are cooked in a mixture of sodium hydroxide, sodium carbonate, sodium sulphide and sodium sulphate. Today this cooking process is continuous. The wood chips are impregnated either at ambient pressure and a temperature of 60 to 70 °C

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[1] Kraft denotates strength or force in German. It is written in small letters.

or with elevated pressure at 110 °C for 10 to 20 minutes The chips are then cooked at 160 to 180 °C and 8 to 9 bar for 0.5 to 2 hours. After the cooking process, the solid and the liquid phase are separated. The fibres are then neutralized with an acidic solution and subsequently washed with water. For the manufacturing of electrical grade pulp, this washing process is of utmost importance, since in this process step any ionic impurities are removed from the pulp. Electrical grade cellulose is normally not bleached; therefore the pulp is dried right after the washing process. The pulp is dewatered in a process that is similar to the paper making process. The dewatering machine consists of a screen-, press- and drying part. The drying part can either be heated rolls or a so called "flash drying" equipment, where the wet fibres are fluffed and blown into a heated chamber where they are dried at a temperature of about 260 °C.

3.2.3 Composition of sulphate wood pulp

In the pulp manufacturing process, lignin and hemicelluloses are partially removed. The typical composition of unbleached softwood kraft is the following:

75 - 85 %	Cellulose
10 - 20 %	Hemicelluloses
2 - 6 %	Lignin
< 0.5 %	Inorganics

3.2.3.1 Cellulose

It is generally accepted that cellulose is a linear condensation polymer consisting of anhydroglucose joined together by glycosidic bonds.

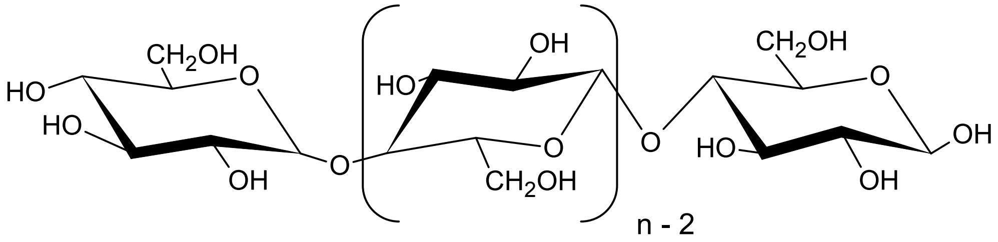


Figure 4: Structural formula of cellulose.

The degree of polymerization - being the average number (n) of glycosidic rings in a cellulose macromolecule - may be as high as 14.000 in native cellulose but the purification procedures, as described above, usually reduce it to the order of 1200 (unbleached soft wood kraft).

When the cellulose molecule is fully extended it takes the form of a flat ribbon with highly hydrophilic hydroxyl groups protruding laterally and capable of forming both inter- and intra-molecular hydrogen bonds. The surface of the ribbon consists mainly of hydrogen atoms linked directly to carbon and is therefore hydrophobic. These two features of the molecular structure of cellulose are responsible for its supramolecular structure and this in turn determines many of its chemical and physical properties.

3.2.3.2 Hemicelluloses

Hemicelluloses substances are a non-uniform group of complex polysaccharides that are not cellulose. Their degree of polymerization is substantially lower than that of cellulose and is between 50 to 250. Hemicelluloses form the actual matrix in which the cellulose fibres are embedded. The hemicelluloses present in the cellulose fibres also play a significant part in the mechanical strength, i.e. in the fibre-to-fibre bonding, because their hydroxyl groups form the hydrogen bridges necessary for chemical bonding.

3.2.3.3 Lignin

Lignin is a complex high-polymeric natural substance that is difficult to degrade. It forms together with the cellulose the main component of wood.

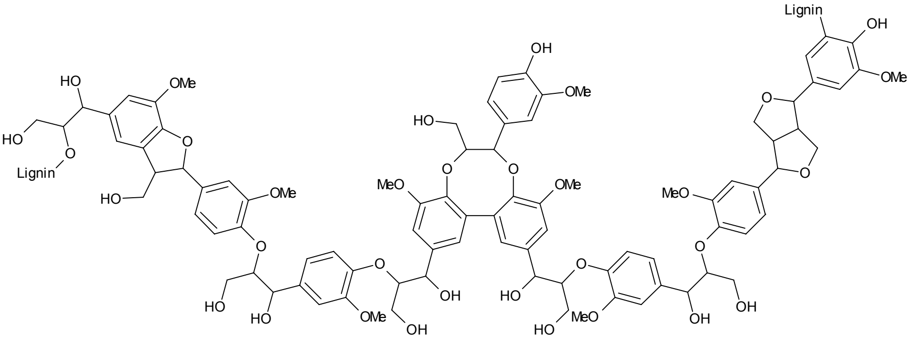
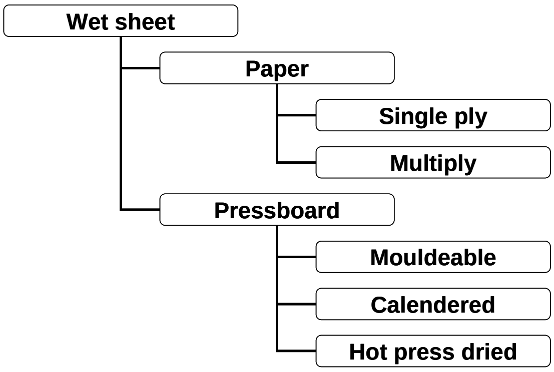


Figure 5: Structural formula of lignin.

3.3 PRODUCTS FOR ELECTRICAL INSULATION

3.3.1 Manufacturing



3.3.1.1 Wet sheet

The initial production process of the paper and pressboard production is identical. The manufacturer supplies the unbleached sulphate wood pulp in a high-purity electrical quality[2]. The cellulose is dissolved in filtered water and temporarily stored in vats. Refining which brushes up the fibres, thus strongly increasing its surface, follows this. At the same time, the

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[2] UKPE = unbleached kraft pulp electrical grade

refining creates very fine ramification, which permits sheets with a very high mechanical strength to be produced.

The treated fibres are further diluted with water and then subjected to intensive cleaning. This cleaning removes not only any metallic or mineral particles present but also any insufficiently opened-up fibre bundles.

The cleaned cellulose-water mixture is now supplied to the sieve of the machine. This filters out the fibres and forms a paper ply. Due to the nature of the production process, the fibres are predominantly orientated parallel to the running direction of the sieve. This causes a difference in properties of paper and board in machine (MD) and cross machine direction (CMD).

3.3.1.2 Paper

Single ply

The paper ply is fed into the pressing and drying section of the paper machine. Finally the finished product is rolled. In separate processes, the paper is, depending on the requirements, calendered, creped and / or slit.

Multiply

For the manufacturing of multi-ply papers, paper machines with more than one former are used. The wet sheets of the different formers are couched together to one layer, which is then fed to the dewatering section of the paper machine.

3.3.1.3 Pressboard

An endless felt carries the paper web from the sieve and transports it to the automatic forming roll. The individual plies are rolled wet on the forming roll to obtain the required wet thickness and are couched without a binder. The wet sheet is separated from the forming roll by cutting.

Mouldable

The wet sheet is fed into the press and compressed. The sheet is then dried without pressure in a continuous oven. Because of its good deformability, this material is used as the raw material for manufacturing of moulded parts.

Calendered

The wet sheet is fed into the press and cold pressed. The sheet is then dried without pressure in a continuous oven. The dried sheets are additionally compressed on a (heated) calender.

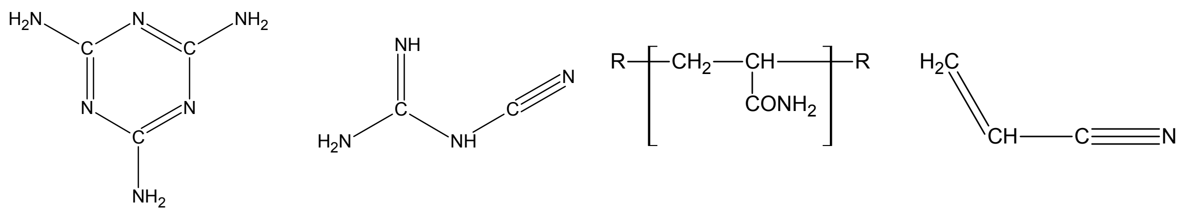
Hot press dried

The wet sheet is dried and compressed at the same time in a heated press under high pressure and at high temperature. The drying parameters are set so that the sheets are dried during the process, providing a very hard and rigid board.

3.3.2 Special treatments

3.3.2.1 Thermally upgrading

The purpose of "thermally upgrading" or "thermally uprating" is to reduce the rate at which the paper decomposes over the lifetime of the transformer. Ageing effects are reduced either by partial neutralization of water forming agents (melamine, dicyandiamide, polyacrylamide) or by inhibiting the formation of water through the use of stabilizing agents (cyanoethylation). The latter method requires modification of the cellulose in the pulp stage and is thus a complicated process and is not used anymore. All processes result in an increased content of nitrogen in the solid insulation, but the treatment is by no means standardised, and the concentration of additives may vary.



Melamine Dicyandiamide Polyacrylamide Acrylnitrile

Figure 6: Agents for thermally upgrading of paper.

A significant advantage of thermally upgraded papers is their better resistance to loss of physical strength in operation. Often, the expression “55 C-rise paper” is used for standard (plain, non-upgraded) paper, whereas “65 C-rise paper” stands for thermally upgraded paper. The numbers refer to the average oil rise temperature, indicating that the designed hot-spot temperature with upgraded paper is higher than with untreated paper. This allows an increased continuous load rating of the transformer.

A wide range of thermal upgrading systems is available[3], and a significant difference between them is the amount of nitrogen used. Because the thermal upgrading chemicals are in most cases not present in kraft pulp, the degree of chemical modification is often determined by testing the amount of nitrogen present in the treated paper. Typical values for nitrogen content of thermally upgraded papers are between 0.5 and 4 percent.

The thermal characteristics of kraft and thermally stabilized kraft paper can be reflected in different thermal classes (105 °C respectively 120 °C), corresponding to the temperature for 50 % reduction of tensile strength after 20.000 hours (IEC 60216-1 and IEC 60216-2).

3.3.2.2 Crepe papers

Insulating crepe papers are made from electrical grade kraft papers. They consist of 100 % pure sulphate wood pulp, and are available in standard or thermally upgraded quality.

Insulating crepe papers are used mainly as wide tapes or cut narrow rolls for insulating parts

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[3] A paper is considered „thermally upgraded“ if it meets the life criteria as defined in ANSI/IEEE C57.100; 50% retention in tensile strength after 65'000 h in a sealed tube at 110°C [Definition draft by ANSI standard].

of the high voltage electrical apparatus. The degree of creping matches to individual requirements, permitting manual or machine wrapping and a close joint between layers. The pronounced mechanical extension characteristics of creped papers enable insulation of rings, bended tubes and conductor leads.

Special mechanically strong crepe papers with high tensile energy absorption are used as a final wrapping around continuously transposed conductor (CTC) bundles.

3.3.2.3 Diamond dot printed papers

Diamond dot printed papers (abbrev. DDP or DPP) are used to form a bonding and insulation system of excellent mechanical stability. In most cases, the resin is applied in dots forming squares, arranged in a diamond pattern and printed to either both sides or only one side of the paper surface. Through oven heating, the thin layer of B-stage epoxy resin[4] melts and cures, providing a bond that is resistant to the solvent effect of transformer oil. The epoxy resin has a superior adhesion to copper and aluminium and is widely used for distribution transformers with the result of solid winding blocks. Occasionally, it is used as a final wrap on CTC conductors of power transformers. These papers are available in standard or thermally upgraded quality.

3.3.3 Products and application (summary)

Table 1: Main components of power transformer insulation.

Solid insulation	Mass (%)	Temp. (°C)	Composition	Material Description (IEC Standard)
Paper (conductor wrapping, soft paper bushing)	20 - 25	80 – 110	Sulphate wood pulp[1]	60554-3-1: 1.1-1.4
Radial spacers (in the winding)	10 - 15	80 - 100	Sulphate wood pulp	60641-3-1: B.3.1
Cylinders and strips (between windings)	15 - 20	60 - 80	Sulphate wood pulp Laminated pressboard[2]	60641-3-1: B.3.1 60763-3-1: LB.3.1.1/2
Corrugated board and cylinder wraps	10 - 15	60 - 80	Sulphate wood pulp	61628 60641-3-1: B.2.1/3.1
Angle rings, caps, snouts, lead exit insulation	5 - 10	60 - 80	Sulphate wood pulp	60641-3-1: B.4.1/5.1
Washer ring plates and spacing blocks	5 - 10	60 - 80	Sulphate wood pulp Laminated pressboard	60641-3-1: B.3.1 60763-3-1: LB.3.1.1/2
Clamping rings and plates	25 - 30	60 - 80	Laminated sulphate wood pulp Laminated wood low density[3] Laminated wood high density	60763-3-1: LB.3.1.1/2 61061-3-1: C1R / C2R 61061-3-1: C3R / C4R
Crepe paper (lead insulation, screen rings, RIP-bushings)	< 5	80 - 110	Sulphate wood pulp	60554-3-3: 3.1 - 3.2
Presspaper[4]			Sulphate wood pulp	60641-3-2: P.2.1/4.1/6.1/7.1
Varnish			Shellac (natural resin)[5]	Shellac

Mass Fraction of cellulosic material in solid insulation system of oil cooled power transformers.
Temp. Refers to typical operational temperature under full load.

1. Alternatively materials made from cotton fibres or a mixture of cotton fibres and sulphate wood pulp are being used.
2. Commonly used adhesives: Casein (water based), synthetic resins (e.g. polyester).
3. Commonly used adhesives: phenolic resins, the reaction product of formaldehyde and phenols.
4. Mainly distribution transformers.
5. In the early years of power transformer manufacturing, Shellac had been applied as a varnish on transformer windings. It is basically a thermoplastic material with a melting point, which increases on prolonged heating, attaining finally a tough and rubbery state.

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[4] This epoxy is solid, but will melt and later cure during heating.

In Figure 7 and Figure 8, insulation components of a core-type transformer are depicted.

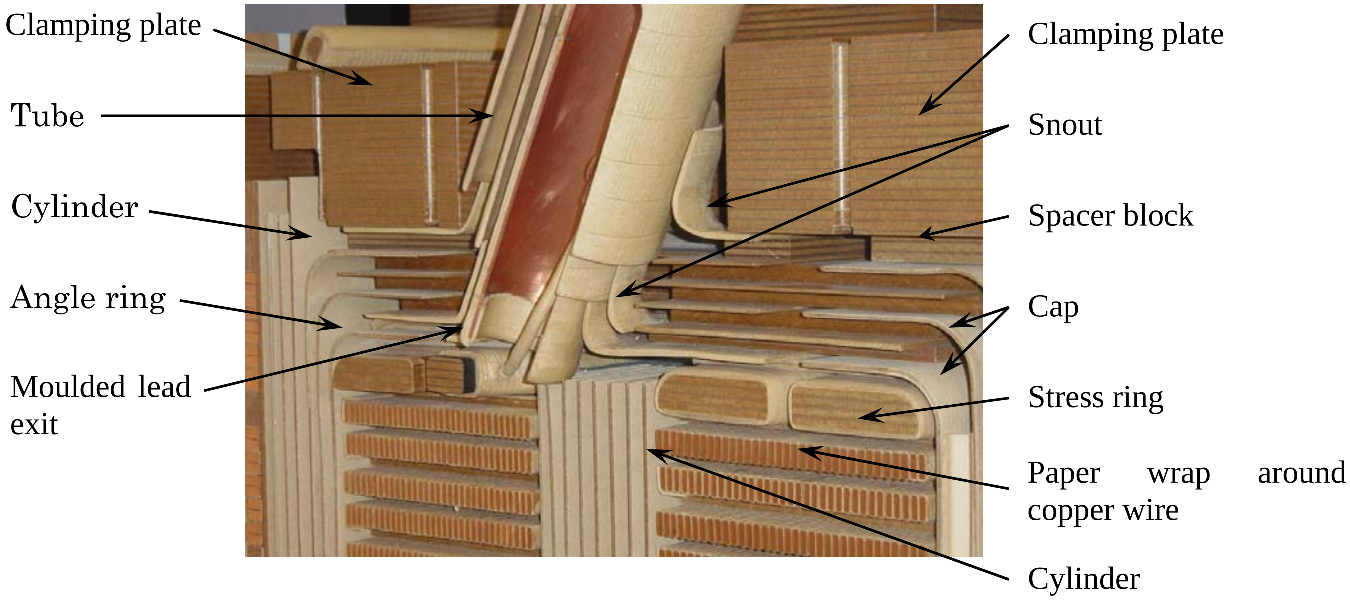


Figure 7: Cross-sectional view of a 400 kV transformer end insulation (220 kV-side).

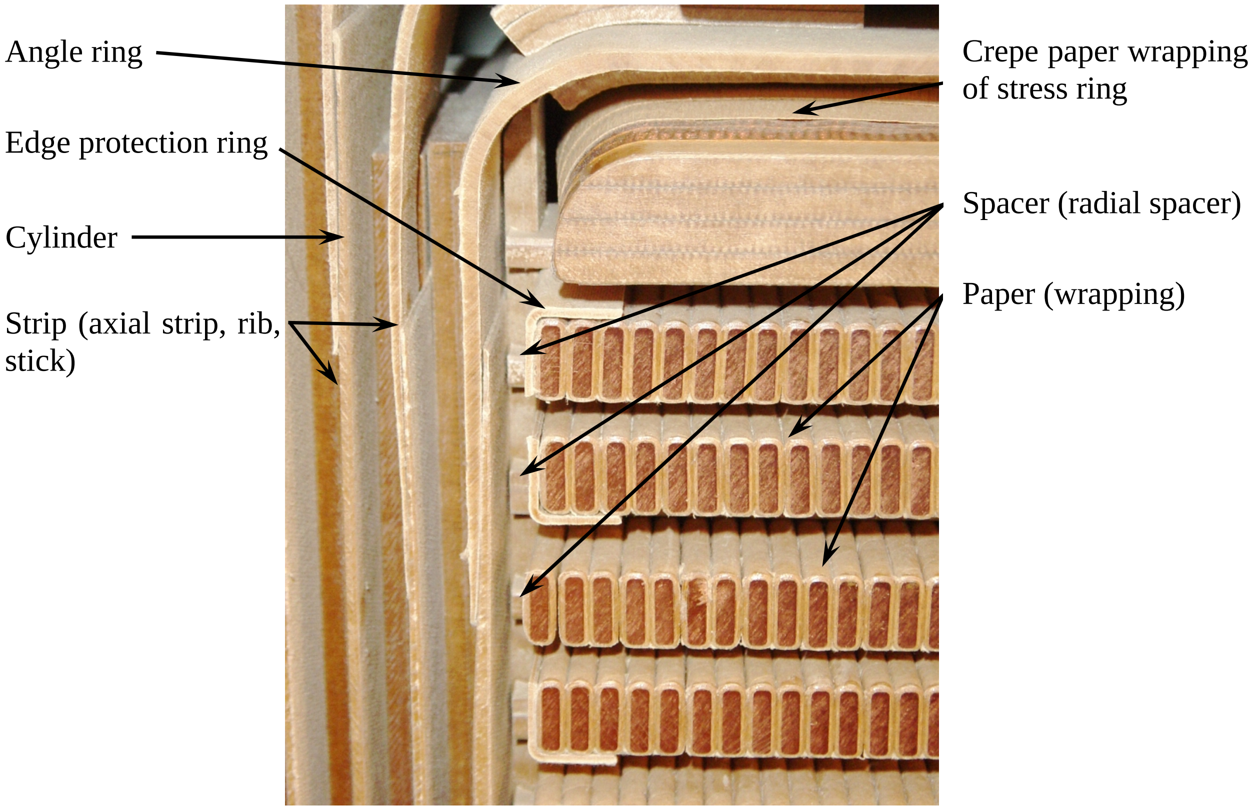


Figure 8: Cross-sectional view of a 400 kV transformer end insulation (detail).

3.4 AGEING EFFECT ON MATERIAL PROPERTIES

3.4.1 Degree of polymerization

The degree of polymerization is measured in accordance with IEC 60450. Since not only cellulose but also hemicelluloses and lignin are dissolved, the DP is a sum parameter. It is a measure for the average molecular weight of the cellulose molecules and so the most important parameter to assess the ageing status of the cellulose insulation of electrical equipment.

With other methods, such as size exclusion chromatography (SEC) not only the average degree of polymerisation, but the molecular weight distribution can be determined.

3.4.2 Tensile strength

The tensile strength of cellulose insulation can be influenced by the choice of raw materials and the manufacturing process. The mechanical strength of insulating paper used for conductor insulation as well as for pressboard used as structural components, plays a vital role for the functioning of electrical equipment. The tensile strength of cellulose insulation materials has a direct correlation to the degree of polymerisation.

3.4.3 Burst strength

The burst strength, which is in fact a biaxial tensile test, shows a similar correlation with the degree of polymerisation as the tensile strength. This correlation gives generally lower values of retained mechanical strength for a particular value of DP than does tensile strength [8].

3.4.4 Elongation

The elongation of the materials is also directly linked to the degree of polymerisation. When the paper reaches its end of life, the elongation becomes very small and thus the paper brittle.

3.4.5 Folding endurance

As the elongation, the folding endurance is also a measure for the brittleness of the material. Its decrease follows the degree of polymerisation similar as the elongation.

3.4.6 Interaction with water

3.4.6.1 Water absorption in air

Saturation (steady state)

Cellulose is due to its chemical nature highly hygroscopic. On the molecular level, cellulose can theoretically absorb 28 % water when all the hydroxyl groups form a hydroxyl bond with one water molecule. In practice the following saturation levels have been found:

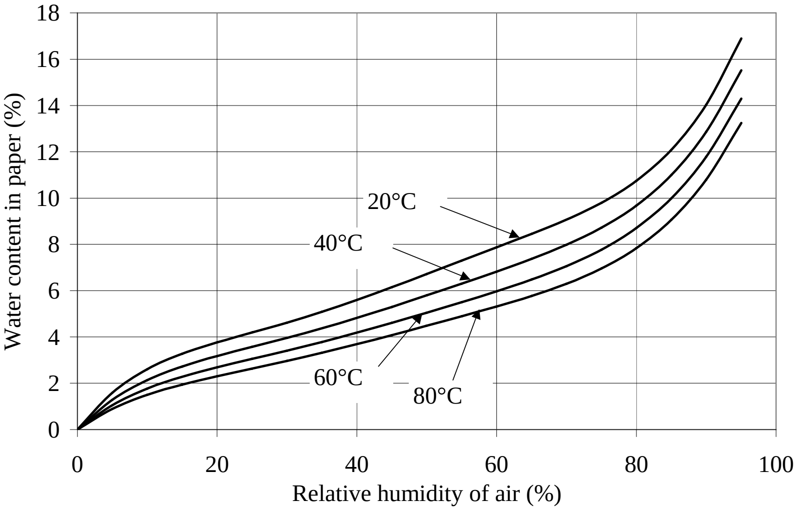
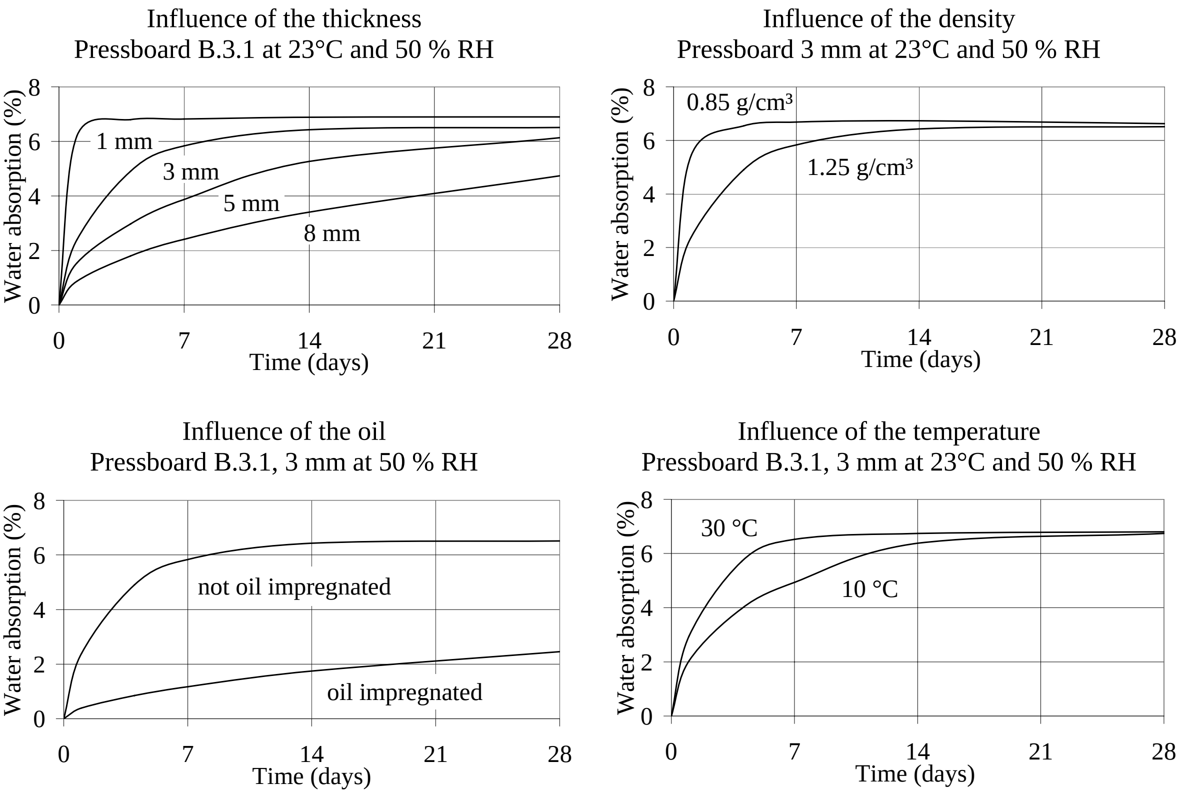


Figure 9: Water saturation of paper in air [after 9].

Rate of water absorption (transients)

The rate of water absorption is governed by the following material parameters:

- Thickness of the board / paper
- Density of the board / paper
- Temperature
- Oil impregnation (without / with oil)
- Environment (air / oil flow)


Influence of the thickness
Pressboard B.3.1 at 23°C and 50 % RH

Influence of the density
Pressboard 3 mm at 23°C and 50 % RH

Influence of the oil
Pressboard B.3.1, 3 mm at 50 % RH

Influence of the temperature
Pressboard B.3.1, 3 mm at 23°C and 50 % RH

Figure 10: Rate of water absorption of previously dried pressboard samples, exposed to air (weight increase) [Weidmann experimental investigation].

3.4.6.2 Dimensional changes due to water absorption

When cellulosic insulation picks up water it swells. The major dimensional change concerns the thickness of the material. In machine and in cross machine direction, the change is about one order of magnitude lower.

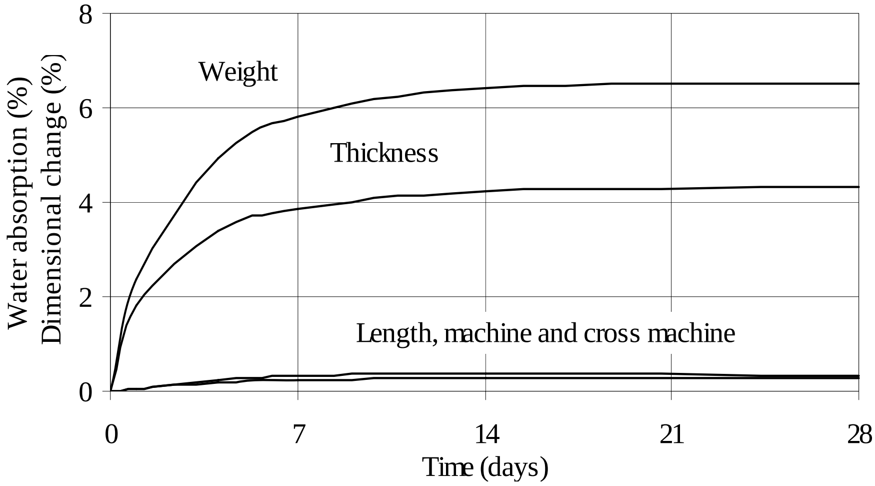


Figure 11: Water absorption (weight) and dimensional change of predried, non-impregnated precompressed board, 3 mm exposed to air at 23 °C and 50 % relative humidity [Weidmann experimental investigation].

3.4.6.3 Moisture distribution in oil filled systems

Insulating oils, such as transformer oil, have a low affinity for water. However, the solubility increases markedly with temperature. In a transformer in service, most of the water stays within the solid insulation. With rising temperatures a small amount of the water moves from the paper to the oil. With the help of the graph below, and assuming the same temperature for oil and solid insulation, it is possible to determine the average amount of water in the cellulose insulation by measuring the water content of the oil [10]. In order to get proper results, it is essential to know the exact temperature of the oil at the moment when the sample is taken. This moisture distribution is only valid for steady-state conditions, which may take significant time to be established. The moisture distribution of aged paper - oil systems will deviate from this as discussed later in 6.1.1.

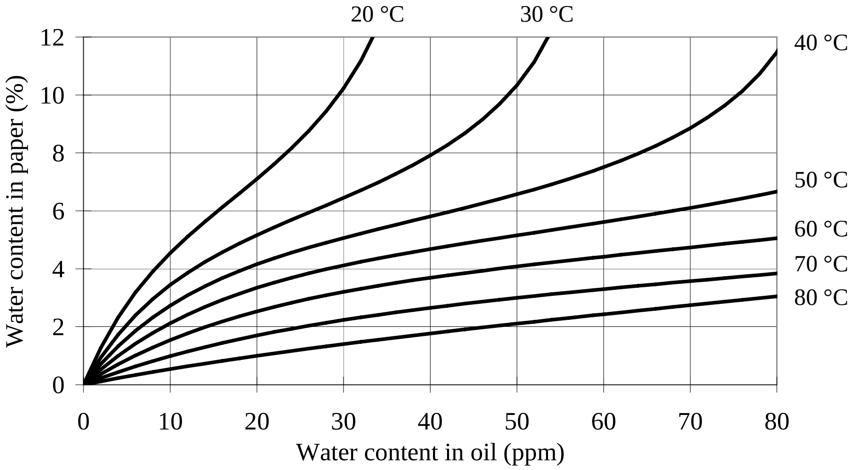


Figure 12: Moisture equilibrium of paper in oil [after 11].

3.5 IEC PUBLICATIONS RELATED TO CELLULOSE MATERIALS

IEC 60216-1 (2001) Electrical insulating materials - Properties of thermal endurance - Part 1: Ageing procedures and evaluation of test results
IEC 60216 -2 (2005) Electrical insulating materials - Thermal endurance properties - Part 2: Determination of thermal endurance properties of electrical insulating materials - Choice of test criteria
IEC 60554 Specification for cellulosic papers for electrical purposes
IEC 60641 Specification for pressboard and presspaper for electrical purposes
IEC 60763 Specification for laminated pressboard
IEC 61061 Non-impregnated densified laminated wood for electrical purposes
IEC 61628 Corrugated pressboard and presspaper for electrical purposes
IEC 61629 Aramid pressboard for electrical purposes

4 AGEING KINETICS – INFLUENCE FROM MATERIALS AND CONDITION

4.1 BACKGROUND; DESIGN AND SERVICE CONDITIONS

The loss of mechanical strength and the ageing of the oil-impregnated cellulosic insulation is one of the important factors that limit the life expectancy of a transformer. It is commonly acknowledged that the ageing is governed by temperature. A lot of research in the last years shows that water and oxygen influence the ageing of solid and liquid insulation significantly.

In many countries the transformer populations have reached an average age around 30 years. Transformers, using normal kraft paper in the insulation, are normally assumed to operate for decades at nominal load under a specified ambient temperature with a design maximum hotspot temperature inside the top of windings of e.g. 98 ^{o}C [12]. With thermally upgraded paper the equivalent hotspot design temperature is 110^{o}C [13]. The ageing of the transformer population accentuates questions concerning life expectancy and good service and maintenance schemes.

Usually the transformers are operated at lower loads than they are specified for. This gives a potential margin in the life expectancy. However, often the condition of the insulation in the transformers is not as good as in a new modern transformer; water, oxygen and contaminants are present and will accelerate ageing.

Ageing depends on temperature; according to Montsinger’s rule - established in the 1930s - life is halved for every 6-10 degrees temperature increase depending on the material [14]. Later, major studies performed by French and British research groups showed that ageing was accelerated by presence of water and oxygen. IEC’s loading guide [IEC 60076-7] does recognize the effects of contamination of the insulation system, but gives no information about its importance. CIGRÉ Task Force D1.01.10 was established to report on ageing of oil-impregnated cellulose, and in this context also maintenance and possibilities for diagnostics. New knowledge has surfaced and needs to be assessed and reported to the transformer manufacturers and users. This Task Force forms one part of the work of CIGRÉ Working Group A2.24 that looks at thermal performance of transformers in a wider perspective, also considering thermal models and designs of transformers and questions concerning operations of transformers in the grid.

4.2 TRANSFORMER INSULATION AGEING

IEC’s loading guide [12] suggests in accordance to Montsinger that the life of a transformer can be described according to the equation:

$$\textbf{\textit{Life duration}} = e^{-p*\theta} \tag{3}$$

where p is a constant (a value 6 is suggested in the range 80-140^{o}C) and θ the temperature in degrees Celsius[5]. This is a simplified version of Arrhenius law used in IEEE’s loading guide [13] stating that per unit life (PUL) can be expressed as:

$$PUL = A \cdot e^{B/(\theta_H+273)} \tag{4}$$

where A and B are constants, θ_H is the hottest-spot temperature[6], which at design hotspot gives PUL equal to one. As no end-of-life criterion for a transformer is available presently,

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[5] Here θ for unit life is set to 98^{o}C, and life halves/doubles for every 6^{o}C up/down.

[6] Note that in this case the reference temperature is 110^{o}C according to US practice of using upgraded paper.

both guides advocate an approach where instead *ageing rates* are considered.

In the IEC guide this reads:

$$\textit{Rate of ageing} = \textit{constant} \times e^{p\theta} \qquad (5)$$

When this is taken further in a relativistic analysis, one then looks at ageing rate at a given temperature compared to that of the design hot spot temperature:

$$V = \textit{ageing rate at } \theta_H / \textit{Ageing rate at } 98^oC = 2^{(\theta_H - 98)/6} \qquad (6)$$

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 reduces the ability of the transformer to withstand short circuit stress. Early work showed how mechanical strength of paper can be measured in several ways as indicated in Figure 13a. Tensile strength, elongation and folding strength all decay with time, and faster at higher temperatures. Plotting the three different parameters against time in semi-logarithmic paper (Figure 13b) shows the same rate of change for all three properties. Some countries also use bursting strength as a reference, tested with a paper spanned over a tube with an internal rubber bladder that is blown up until the paper bursts. Bursting strength is reported to have a more linear correlation with DP [8,15] as seen in Figure 14.

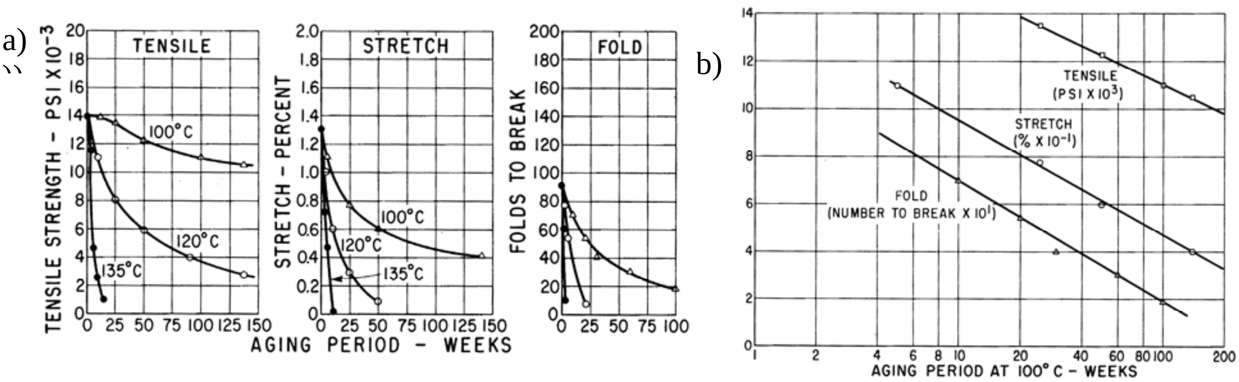

Figure 13: a):The effect of temperature on three representative mechanical properties of vacuum dried and oil impregnated insulating paper aged under oil in sealed containers having nitrogen gas in contact with the surface of the oil [16]. b) Comparison of the three mechanical properties, showing equal ageing rate for all three properties. The same is valid at 120°C and 135°C.

Because it is impossible to perform meaningful mechanical tests on paper samples unwrapped from conductors in a transformer one is stuck with the possibility of measuring the *degree of polymerization* (DP) of such samples [18,19,20]. 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 [17]. For new paper the DP-value is about 1200, and after a new transformer has undergone high temperature drying a DP-value around 1000 is representative. With other methods, such as size exclusion chromatography (SEC) not only the average degree of polymerisation, but the molecular weight distribution can be determined as shown in Figure 15 [18, 19].

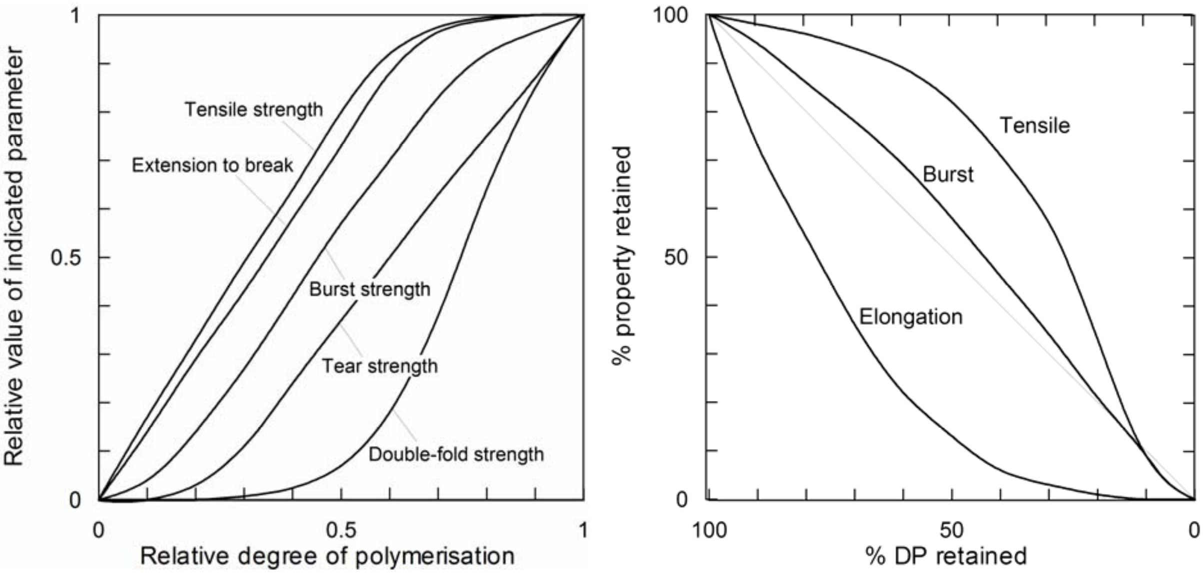

Figure 14: (a) Relative decrease of mechanical parameters with decrease of DP of cellulose paper. Redrawn after [15]. (b) Correlation between mechanical properties and remaining DP of upgraded creped kraft paper. Redrawn after [8].

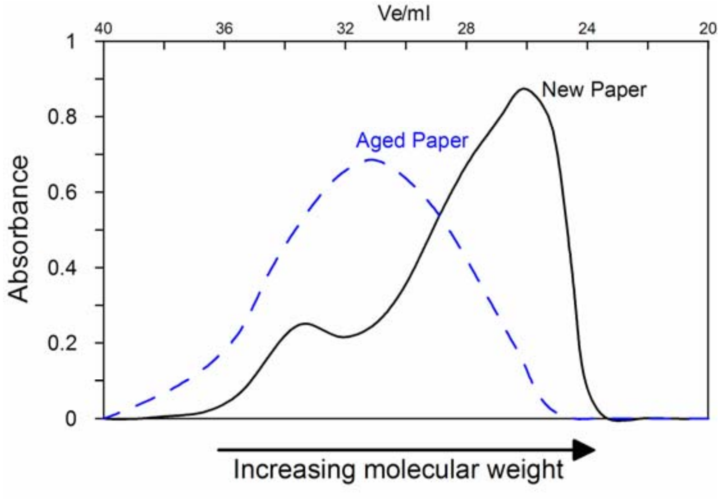

Figure 15: Molecular size distribution of new and aged kraft paper. The measurement is done by gel permeation chromatography (GPC) and light absorbance. X-axis is elution volume [ml]. For new paper, the right peak is the cellulose, while the left peak probably shows hemicelluloses. **[**Investigation by Dr David Hill, University of Queensland].

During ageing both mechanical properties and DP-value will be reduced with time as shown in Figure 16. The figure also shows how the tensile strength depends on the polymerisation of the paper. Often a DP value of 200 is considered as the end-of-life for the cellulose insulation. Figure 16c shows that at this DP level the tensile strength is about 30 % of initial. Interfiber forces are also reduced when DP is getting down in this range; the ratio between long-span to short-span tensile strength falls [20]. Here long span and short span refers to the distance between the jaws of the tensiometer; long span involving a longer paper strip with more bonds between fibres than for the short span where the jaws are very. Down to DP-values of 600-700 the papers mechanical strength will stay as for new.

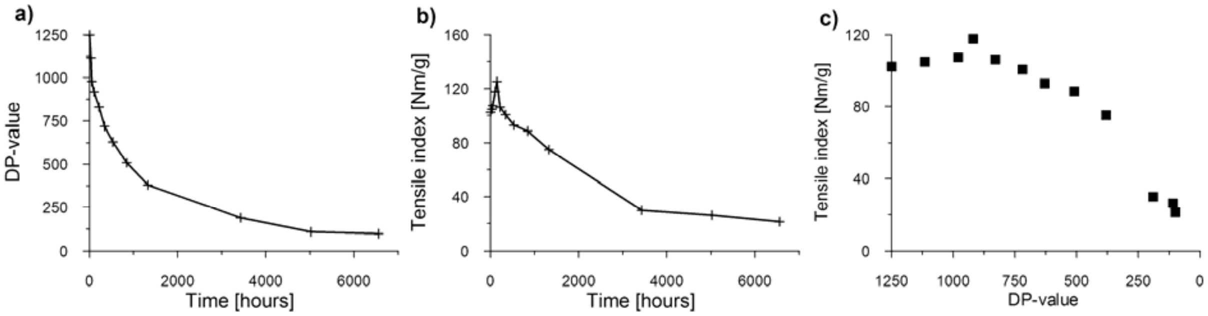

Figure 16: Development of DP and tensile strength of paper for ageing kraft paper (3% water at 110^{o}C), and correlation between the two parameters from multiple experiments [21].

4.3 PAPER DEGRADATION; THE GENERAL KINETIC MODEL

As ageing proceeds the molecular weight and DP of the cellulose is reduced due to molecular cellulose chains being cut. The relation between the chain scissions (η) and measured DP is:

$$\boldsymbol{\eta = DP_0/DP_t - 1} \qquad (7)$$

DP_0 is the initial degree of polymerisation and DP_t is value after an ageing period t. Most analyses of degradation have been based on the work of Kuhn and co-workers in 1930 [22], which was extended by Ekenstam in 1936 to relate rates of degradation to DP [23]. Ekenstam considered random, first order chain scission and showed a direct relationship of reciprocal DP with time and that this relation combined with the Arrhenius equation to include temperature dependence can be mathematically expressed as:

$$\frac{1}{DP_t} - \frac{1}{DP_0} = A \cdot e^{\frac{-E}{RT}} \cdot t$$

$$(8)$$

$$\frac{1}{DP_0}\left(\frac{DP_0}{DP_t} - 1\right) = A \cdot e^{\frac{-E}{RT}} \cdot t$$

Here, R is molar gas constant (8,314 J/mole/K), T the absolute temperature in Kelvin (equal to θ_H + 273) and E is the *activation energy* in kilojoule per mole. A is a constant depending on the chemical environment.

So from several reasons it is convenient to focus on changes in the DP value or the rate at which chain scissions occur. The equation above can be explained and supported by the following procedure and considerations: If we instead of plotting DP vs. time as shown in Figure 17a, plots 1/DP as shown in Figure 17b we get fairly straight lines, showing that the rate of change (k) is quite linear over time up to a certain value of 1/DP. This is in accordance with a model saying that $\Delta\eta/\Delta t = k$, which is a first order reaction rate model. Plotting the natural logarithm of k vs. 1/T gives straight lines as would be the case for a thermally activated process described in an Arrhenius plot. In equation 6 it is the value of E describes the slope of the curve in Figure 17c; the higher this value is the more temperature dependent will the reaction rate be (steeper curve). Table 2 shows how the activation energy is related to the temperature increase giving a 50% life reduction: Chemists prefer to relate the energy to joule per mol, while physicists use eV per molecule. In principle the *A*-values determine the intercept of the curves in 14c with a virtual Y-axis from 0; the higher the value the higher the location of the curve above the abscissa and the faster the ageing.

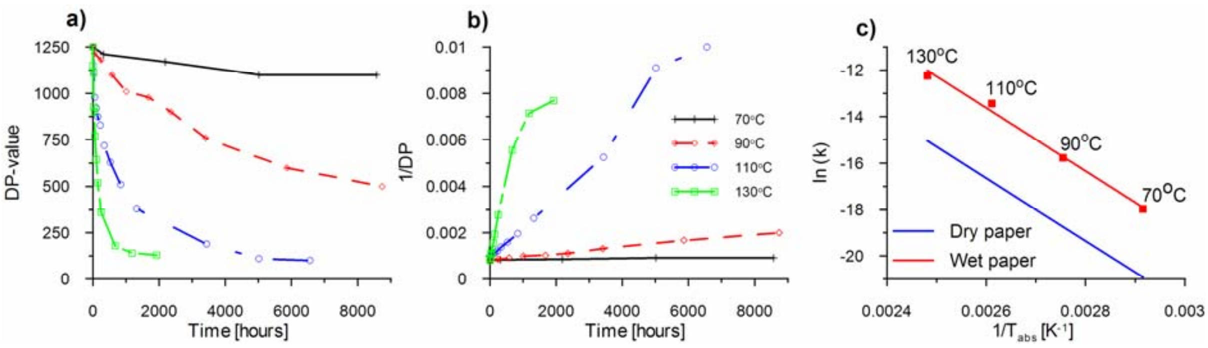

Figure 17: Ageing of kraft paper with a high initial water content versus time for four different temperatures. a: DP-value versus time, b: 1/DP versus time, c: Reaction rate versus inverse absolute temperature [21]. (Wet paper is real data, dry paper is somewhat idealised; i.e. assuming an activation energy equal to that of wet paper.)

Knowing the end-of-life (EOL) criterion, we can reorganize equation 6 to express life expectancy as a function of temperature T, and the parameters E and A:

$$Expected\ Life = \frac{\frac{1}{DP_t} - \frac{1}{DP_0}}{A * 24 * 365} * e^{\frac{E}{RT}} \ [year] \qquad (9)$$

Which is equal to what was is suggested in the standards, except from the EOL-criterion being based on DP value instead of mechanical rigidity of the paper as Montsinger did.

Table 2: Correlation between activation energy and temperature rise for halving of life. This is only valid in a limited temperature range around maximum operating temperature.

Activation energy	kJ/mol	70	90	110	130	150
ΔT (50%)	°C	11,7	9,1	7,4	6,2	5,4

4.4 STRUCTURE OF CELLULOSE AND THE REACTION RATE

The structure of cellulose is also said to influence the rate of degradation. In the fibers and micro-fibers the cellulose is found in semi-crystalline regions where these regions of high crystallinity are separated by regions of low crystallinity or amorphous structure. The amorphous regions are said to degrade quicker than the more crystalline regions (Erofeev et al., 1982) and even in the amorphous regions there are said to be areas that are more reactive than others. The existence of weak links within the cellulose chain have been proposed to explain initial rapid degradation rates before a steady rate was achieved [24, 25, 26, 27, 28, 29]. A weak link where the cellulose chain folded (every 30 units) was proposed by Chang [24], which coincided with the fibril lengths of 30 nm. Other reports have suggested a weak link every 500 units [26]. The degradation rate of crystalline regions of cellulose is lower due to the higher degree of order within the cellulose chains reducing accessibility of ageing agents and the increase in strength induced by crystallinity. During ageing one can see that the DP reduction levels off at a value of about 100. At this level, only microcrystalline regions of the cellulose remain[7].

Looking closer to Figure 17b one sees that the curve describing the reaction rate at 130 ^{o}C is not straight. The steepness (or reaction rate) falls off with time. This is explained by a reduction with time of amorphous regions or locations in the cellulose structure where chain scissions may occur. In a recent study [30] it is proposed to extend Equation 6 to:

$$\frac{1}{DP_t}-\frac{1}{DP_0}=\frac{k_{10}}{k_2}\left[1-e^{-k_2 t}\right] \tag{10}$$

Where k_{10} is the initial rate at which bonds break and k_2 is the rate at which k_{10} changes. k_{10} and k_2 will vary with temperature in the same manner using the Arrhenius equation. Equation 8 takes into account that the rate of chain scissions changes with time as would be expected for an inhomogeneous material such as kraft paper, with a mixture of amorphous and crystalline regions.

In addition to the cellulose also hemicellulose and lignin will age. The lower “hump” in Figure 15, is associated to the hemicellulose. One can see that also these molecules are reduced in size with ageing.

4.5 DEGRADATION PROCESSES

The degradation of paper insulation within transformers has been studied for many years and several theories postulated on the mechanism and the kinetics involved. It is commonly accepted that the main factors influencing the degradation paper insulation are temperature, water, oxygen, acids and contaminants.

There are many reports in the literature that have tried to quantify the degradation rates with respect to water, oxygen and temperature. These reports have been reviewed for transformer operating conditions by Emsley [31, 32, 33]. Other factors such as electric fields and oil degradation products are considered to be of secondary importance according to Fabre and Pichon [11].

The temperature at which a transformer operates will affect the rate of degradation. The rate of most chemical reaction rates doubles every 2-25°C, depending on the activation energy. Reported activation energies for cellulose aged in oil vary from 85 kJ/mol [34, 35] (degradation in vacuum) to 120 kJ/mol [36] (hydrolytic degradation). Emsley [31] calculated an average activation energy of 111 ± 6 kJ/mol from results from the main significant studies available at that time, using the assumption that the rate of degradation approximates to zero order and that all processes have the same activation energy. However, biotechnologists state that normally hydrolyses have an activation energy in the 115-130 kJ/mol range and oxidation via free radical influence give activation energies in the 50-65 kJ/mol range [37]. It has been reported that the rate increases significantly above 140°C [38], due to a change in the activation energy or the pre-exponential factor of the Arrhenius

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[7] Actually, microcrystalline celluloses used as filler in medical tablets is produced by hydrolysis of cellulose.

equation. For ageing in a water and oxygen free environment, where only pyrolysis takes place activation energies are found to increase; Fung doing experiments under vacuum at 200 to 280^{o}C experienced activation energy of about 150 kJ/mole [39] and even higher values are suggested. Potential oxidation of the paper greatly effects the pre-exponential factor [31]; i.e. any residual oxygen in a so called oxygen free environment will effect the Arrhenius parameters significantly. Zou et al. [40] associated an increased rate above 140°C with pyrolysis (thermal degradation) of cellulose and assumed that below this, the dominant mechanism is hydrolysis.

To summarize: One may say that we have three main processes of degradation:

- Hydrolysis
- Oxidation
- Pyrolysis

In a real transformer all these processes – hydrolysis, oxidation and pyrolysis act simultaneously, resulting in a non-linear Arrhenius plot - which hampers the application of one single activation energy - describing the full complexity of the degradation processes. Which process will dominate depends on the temperature and the condition. Probably also synergetic effects takes place between the different reactions; e.g. oxidation may activate hydrolysis. However, we will for illustrative purposes assume independent processes. The total degradation then being the sum of degradation from each process becomes:

$$\eta_{Tot} = \left(A_{Oxi}\, e^{\frac{-E_{Oxi}}{R \cdot T}} + A_{Hyd}\, e^{\frac{-E_{Hyd}}{R \cdot T}} + A_{Pyr}\, e^{\frac{-E_{Pyr}}{R \cdot T}} \right) \cdot t \qquad (11)$$

where *oxi*, *hyd* and *pyr* are used as subscripts to identify the activation energy *E* and the environment factor *A* for the singular processes mentioned above. Somewhat simplified one can say the degradation rates from these reactions will depend on activation energy and the environmental for each process at the given temperature. The ageing rates dependence on temperature will vary depending on which process that dominates in the specific region as suggested in Figure 18.

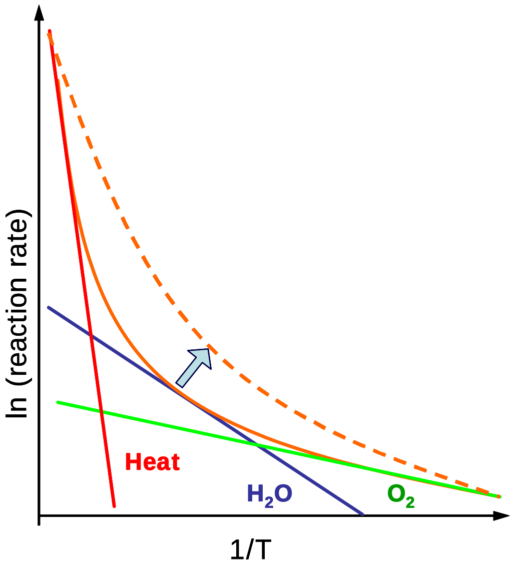

Figure 18: Sketch of ageing rates due to different ageing mechanisms. The arrow shows the effect of increased water content increasing the A-factor for hydrolysis.

4.5.1 Hydrolysis

Presence of water will increase the rate of degradation. At the beginning of a transformer's life, the kraft insulation contains less than 0.5 % water, and the oil is also dried. The water content levels within the transformer may increase up to 5 % during its lifetime (Fallou, 1970). Fallou (1970) showed that the rate of degradation of the paper at initial value of 4% water content was 20 times greater than that at 0.5 % water content. So, in principle as the transformer ages the rate at which the insulation deteriorates is expected to increase. Recently, Lundgaard et al [41] suggests that the hydrolysis of cellulose is a catalytic process where the reaction rate depends on dissociated acids or rather H^+-ions that can get into the amorphous zones of the cellulose. This mean that the A-factor will depend both on the existence of organic acids - as earlier also suggested by Ivanov [42] – and water, that is able to dissociate these acids. Low molecular weight watersoluble acids, that are formed by the paper ageing and to some degree also by the oil ageing, are more efficient than the larger hydrophobic acids, which mainly stems from the oil ageing. The fact that acid catalyzed hydrolysis generates organic acids and at the same time is governed by their presence makes the process auto-acceleratory.

4.5.2 Oxidation

Oxygen will also accelerate the degradation reaction. If the oxygen level in the oil is held below 2000 ppm the rate of degradation of the full insulation system is reported to be five times lower than that of a free breathing transformer [43]. Transformer oil can reach about 30 000 ppm when the oil if fully saturated, but in reality most free breathing transformers in service (warm) only contain 20 000 ppm as a result of dissolution of gas from the air. Cox' results suggest that by extracting the oxygen to below 300 ppm, using for example semi-permeable membranes the effect of oxygen can be reduced to a sixteenth of that of normal operating conditions [44]. These results contrast with experimental evidence that ageing of paper in oil with access to oxygen is only about 2-3 times higher than ageing under vacuum [11, 41]. Oxidation promotes accumulation of additional ageing accelerators as e.g. acids.

It is suggested [41] that the oxidative depolymerisation is catalyzed by hydroxy-radicals (HO•), which are produced by decomposition of hydrogen peroxide, H_2O_2 and of organic hydroperoxides (ROOH). Hydrogen peroxide can for example be formed from oxygen and water by reactions catalyzed by transition metal cations (such as Cu^+/Cu^{2+} or Fe^{2+}/Fe^{3+}). Hydroxy-radicals are formed from H_2O_2 or ROOH in a reaction catalyzed by traces of Fe^{3+} or other active metals, together with small amounts of autooxidizable compounds such as phenols, aromatic amines or thiols. It is here also suggested that the oxidation is reduced in an acidic environment, which would reduce the importance of these reactions with time.

4.5.3 Pyrolysis

By pyrolysis we mean a process that can take place without access to water and/or oxygen, or any other agent to initiate the decomposition. At normal operating or overload temperatures (i.e. $<140^oC$) such processes are considered to be of little relevance. At high temperatures, which may occur at defects such as poor soldering or magnetic induced local failure currents, pyrolysis may well occur. Generation of CO and CO_2 may follow. However this is outside the scope of this report.

4.5.4 Influence from oil

Liquids for transformers are mainly mineral oils, with different composition and refining, containing different oil molecules (aromates, naphtenes and paraphines), sulphur compounds, inhibitors, passivators, etc. Also synthetic liquids like vegetable and mineral oil based esters, silicone oils etc are used. In principle ageing products from these liquids may influence the paper ageing.

Hydrolysis may be influenced by low molecular weight acids from oils. Oxidation of the oil produces both low molecular weight acids and larger acids. Oil testing according to IEC [45] includes measurement of both high and low molecular weight acids in the aged oil and in a water trap respectively, so in principle data on this is available. However, it seems that a significant fraction, or even most, of the low molecular weight acids found are paper degradation products.

In their book, Lipstein [46] et al. describe oil ageing in general and also the influence on paper ageing. Their focus was mainly on transformer oils from Russian crude oils. They suggest that in a process of autocatalytic oxidation of hydrocarbons polyatomic hydroperoxides are formed, which as explained above through the reaction with copper would form radicals that would initiate oxidation of paper. They observed that paper ageing in synthetic askarels was slower than in mineral oils, and attributed this to less production of aggressive compounds in these liquids.

It has been suggested that paper will age slower in certain esters due to a drying effect of the liquid due to its higher (some 100 times) water solubility. This is believed to be a highly unlikely effect, as anyway the solubility of water in cellulose will be much higher than in the ester, and the water concentration in the paper in a real transformer - having a weight ratio oil/cellulose of 10-20 - would not be that much influenced.

However, even if we know that there is a correlation between oil and paper ageing, much of this is still not properly investigated. Here one should not forget that the additional complication of the environment with metals in the real transformer.

4.6 AGEING OF CELLULOSIC INSULATION IN TRANSFORMERS

4.6.1 Kraft paper

For kraft paper the general picture is that ageing rates doubles for every 6-8 degrees Celsius. Based on equation 7, a start DP=1000 and end-of-life DP=200, paper would last about 20 years at a temperature of 98^{o}C using an A-value of $1\cdot10^{8,}$ which has been found representative for test conditions where access to oxygen and water is hindered. Free access to air and oxygen would reduce expected life with a factor of about two. How this reduction depends on the content of oxygen in the oil is not clear. Life expectation is approximately inversely related to water content and at around 2% the life would be reduced by a factor of around 10. One knows that there is a strong synergy between water and organic acids, but details on how to assess this synergetic effect are not yet known.

In his thorough review of paper ageing Emsley found an activation energy of 111 kJ/mol, with 95% confidence bounds of 105-117 kJ/mol, in average for all the experiments reviewed. The same value (114kJ/mol) Lundgaard found by mapping a large group ageing experiments together. However, he found that when differentiating between experiments where oxygen was added and those where water was added he got respectively 96 kJ/mol and 125 kJ/ mol, supporting the idea that the activation energy is different for the oxidation and hydrolysis.

Based on choosing an activation energy of 111 kJ/mol for ageing of cellulose under optimum conditions an A value of 1 to 2×10^8 seems reasonable.

Figure 19 shows how water will influence the A-values based on the findings of Emsley from [31] (with 95% confidence limits) and data from [41]. Note that it is the region of water contents up to 2% which is of most practical interest, since at equilibrium conditions higher water contents than this in the hottest regions of the windings are very unlikely.

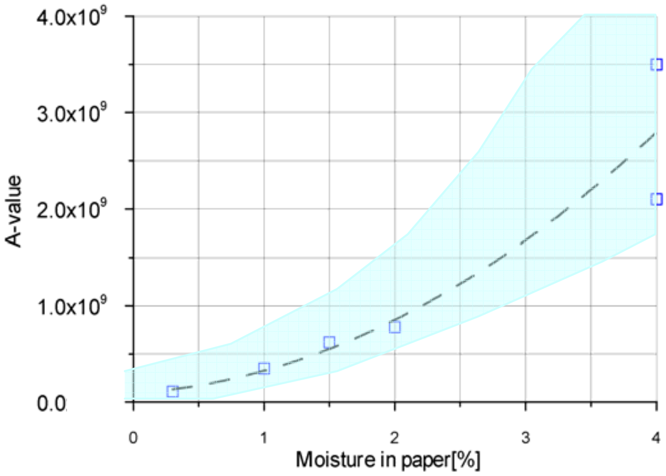

Figure 19: Ageing factor ”A” for initial water content in cellulose in laboratory tests. The unit of A is h^{-1}.

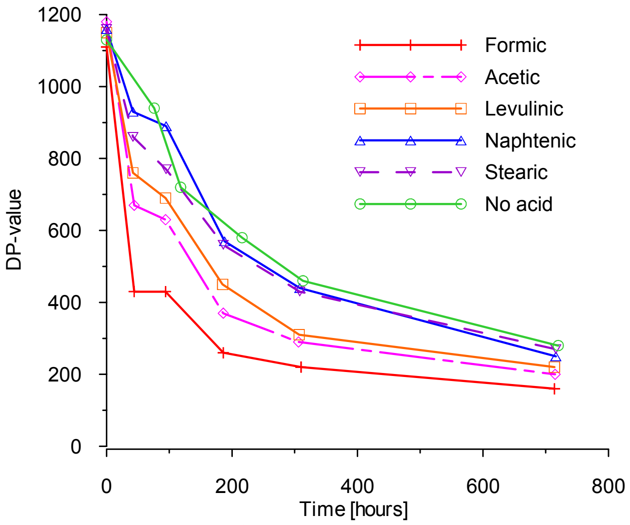

Figure 20: Ageing of kraft paper at 130°C with 2,5 % water content with different acids in oil. The oil was prepared to a neutralisation value of 0,4 mg KOH/g oil before impregnating the paper with it. Formic, acetic and levulinic acid were to a large extent absorbed by the paper, while naphtenic and stearic were not absorbed [47].

The direct correlation of ageing rate to water content can only be considered a preliminary step as acids do play a role together with the water. It is known that low molecular acids together with water are the real driver of the hydrolysis, potentially being the most significant process [42, 47]. One would expect that a relation like $A \propto K_{H2O} \cdot N_{LA}$, where K_{H2O} is the concentration of water in cellulose and N_{LA} is the neutralisation value of low molecular acids in the oil or paper, to be a potentially better parameter for assessing the importance of hydrolysis. Figure 20 indeed supports the focusing on the low molecular acids. One must be aware that in this study the partitioning coefficient of the various acids resulted in very different acid concentrations in the paper. This is in line with experiences from service aged transformers, where the concentration of water soluble acids can be 100 times higher in the paper than in the oil. It is clear that the high molecular weight acids not being water dissolvable and mainly originating from oxidation of oil – which dominates the neutralisation value of the oil – do not play any significant role for the cellulose ageing. However, much work remains before a more practical A-value for the cellulose ageing can be determined from oil diagnostics. The neutralisation value (total acid number) – as used today- is not good for assessing the content of low molecular weight acids in the paper.

A hypothesis emerges – at least for open breathing transformers – that the ageing starts with oxidation in an alkaline or neutral environment. With time, this process is limited as the environment becomes more acidic and the auto-accelerated acid catalyzed hydrolysis takes over.

4.6.2 Thermally Upgraded Paper

Thermally upgrading of paper may reduce the ageing rate by a factor between 1,5 and 3. The ageing acceleration from the presence of water is seen to be strongly reduced for the upgraded paper, while ageing with access to oxygen seems to be less influenced. For upgraded paper there is still some uncertainty about the activation energies, and which process dominates ageing. The reduced sensitivity for hydrolysis is in line with theories presented by Bauer et al. [48], and are supported by two larger investigations performed by Shroff [49] and Lundgaard [41, 50]. In these investigations paper from two different manufacturers was used.

Lundgaard et al. have shown that upgraded paper produces more acids than regular kraft paper. This effect has to be verified in further experiments. Lundgaard found that the activation energy for the ageing of upgraded paper was lower than for kraft. Most likely the ageing of the paper he investigated is mainly caused by oxidation, due to the alkaline environment provided by the additives that would favor oxidation and sequester the acid catalyzed hydrolysis.

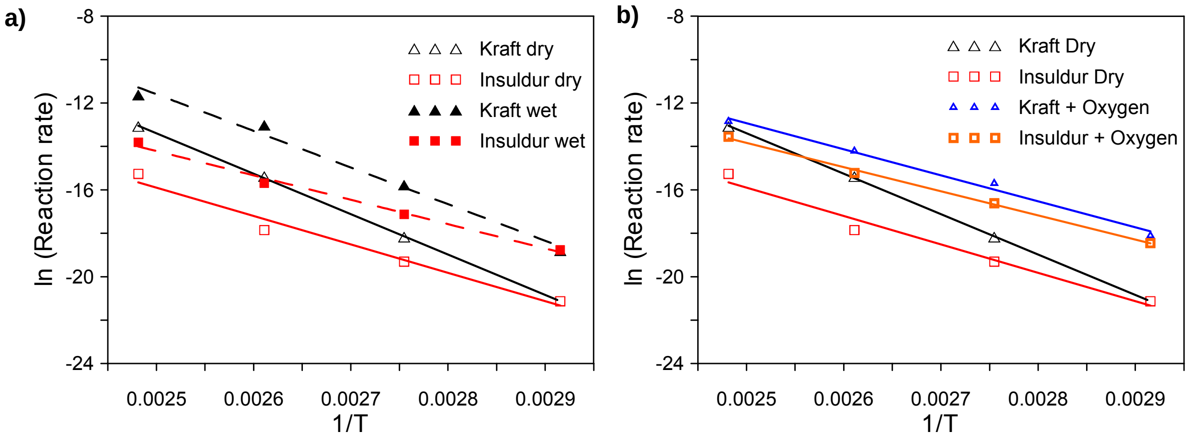

Figure 21: Arrhenius plots from ageing experiment on kraft and Insuldur paper: a) influence of 3% water and b) influence of oxygen [50]. Values are taken from the initial slope in the 1/DP plot.

4.6.3 Ageing of wood

In today's power transformers, substantial quantities of laminated wood (commonly called "plywood") are often used, replacing laminated pressboard products mainly for economic reasons.

Laminated pressboard is produced by laminating individual sheets of high-density pressboard together with either a synthetic (polyester resin) adhesive or casein glue [51]. In contrast, laminated wood is produced by joining pieces of wood veneers (typically beech) together with a thermosetting synthetic adhesive (typically phenolic) under pressure and heat. There are many grades of laminated wood products available for the transformer industry. These depend on the density of the wood and the directionality of the beech veneers [52]. Due to the following parameters, these two materials behave differently:

- Lignin content
- Microscopic structure of the fibers
- Macroscopic structure of the sheets
- Type and amount of adhesive

Despite the composition of these wood products being quite different from kraft presspaper and pressboard, there has been done very little ageing research with laminated wood in the past. Yet, a recent study has discovered interesting test results [53]. Two different types of laminated wood (low and high density) from two different suppliers were tested in parallel with laminated pressboard at temperatures from 105 to 135 °C, and an ageing time of up to 16 months. Regular testing of the condition of the liquid and solid insulation included flexural strength, water and acid contents.

To sum up:
Laminated pressboard showed a significantly better ageing performance than laminated wood:

- Laminated wood can produce aggressive, corrosive acids – explaining problems with vapor phase systems (corrosion of pipes and valves), as reported repeatedly by the transformer industry. Moreover, acids accelerate the ageing process of all cellulosic insulation.
- Solid ageing by-products from laminated wood can clog cooling ducts, in the worst case causing premature paper ageing due to elevated temperatures.
- The mechanical strength of laminated wood deteriorates more rapidly than the strength of laminated pressboard.
- The pronounced water production by laminated wood ageing reduces the electric strength of the oil, and accelerates the ageing process of all cellulosic insulation.
- High gas production of wood at elevated temperatures can cause dangerous bubbling, e.g. during temporary overload condition, which in turn can lead to partial discharge (PD) inception. In consequence, this effect limits the thermal overload performance.
- Despite the fact that the laminated woods test samples were all in accordance with the corresponding IEC specification [52], the materials showed significant differences in their ageing behavior.
- Another not to be neglected fact is that due to the nature of laminated wood fabrication (veneer patch work), the inclusion of voids is inevitable. In the case that such voids are not impregnable with oil because they are completely surrounded by adhesive, PD-inception at low electric fields is the consequence - with hazard of catastrophic breakdown early or after years in operation.

4.7 IEC, IEEE AND CIGRE PUBLICATIONS RELATED TO AGEING KINETICS

IEC 60076-7 (2005)	Guide for loading of oil-immersed transformers
IEEE Std C57.91-1995	IEEE Guide for loading Mineral-oil-immersed Transformers
IEC 60450	Measurement of the average viscometric degree of polymerization of new and aged electrical papers
IEC 61125	Unused hydrocarbon based insulating liquids - Test methods for evaluating the oxidation stability
IEC 61061	Non-impregnated densified laminated wood for electrical purposes

5 DEGRADATION PRODUCTS IN IMPREGNATED INSULATION SYSTEMS

5.1 INTRODUCTION

The ageing of paper and board leads to the formation of many different products. All the main constituents of paper, *i.e.* cellulose, hemicellulose and lignine, will degrade. Many different degradation products will be formed. Some are fairly stable, others may degrade further. Some of the most important degradation products will be briefly discussed in this section, from different points of view.

In theory, the ultimate degradation products of cellulose are water and carbon oxides. Obviously, in real life no transformer can be operated up until the point where all paper components are totally degraded. To be strict, in a real transformer at the end of technical life the main degradation product is in fact slightly modified cellulose. However, this fills the same function as the unaged material, and what concerns us are mainly what could be described as by-products. A degradation product is discussed in this section if it meets one ore more of the following criteria:

- Its presence may constitute a threat to the safe operation of the transformer
- It affects the ageing rate of the insulating system
- It can be used as an indicator of ageing, or has some other diagnostic value.

Another aspect that deserves to be stressed is that the oil and the solid insulation will age together. Sometimes a certain product can be formed from either of them. Furthermore, any degradation product, regardless of its origin, paper or oil, will be found in both (although the distribution may vary much from case to case). Also, the degradation products of one may affect the degradation of the other. For these reasons it is not possible, nor meaningful, to keep at all times a strict distinction between paper degradation products and oil degradation products.

5.2 DEGRADATION PRODUCTS FROM CELLULOSIC INSULATION MATERIALS

5.2.1 Water

Water is a dominant degradation product of paper and board. It is formed by dehydration reactions following hydrolysis (which itself actually consumes water), but is also an end product in the oxidation of oil as well as that of paper. The amount of water formed may constitute several % by weight of the total mass of solid insulation. Figure 22 shows the amount of water formed in laboratory ageing experiments, as a function of the number of chain scissions of the cellulose chain.

Most of the water that is formed is retained in the solid insulation. Typically less than 1% of the total amount of water is dissolved in the oil. Some examples of equilibrium curves are shown in Figure 23. The distribution of water between paper and oil is discussed in more detail in chapters 5 and 7.

Substantial amounts of water may also be the result of ingress from the outside. This, together with others aspects of water in transformers, has been discussed in detail in the report of CIGRE WG 12.18 [54].

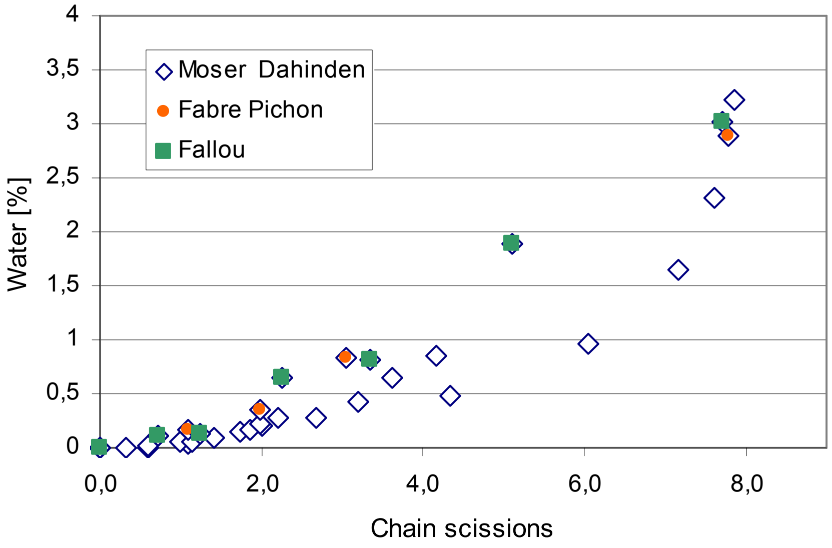

Figure 22: Water production during degradation of oil impregnated cellulose insulation. The curves represent excerpts from several experimental studies [2,11,35].

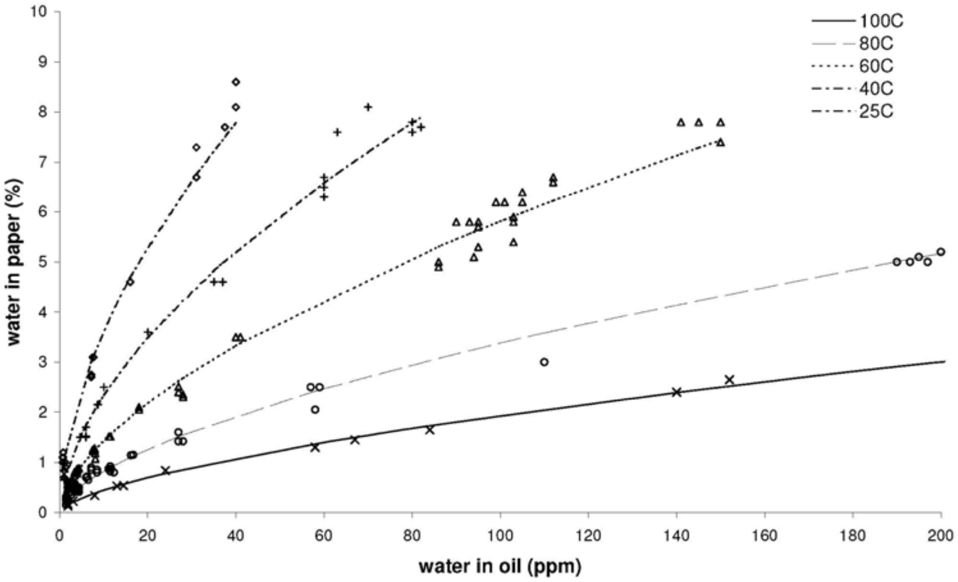

Figure 23: Some experimental curves for water in oil (Nytro 10X) *vs*. water in paper (Munksjø) for different temperatures. Data from study carried out by Spicar, 1972 on unaged paper and oil. These curves do not necessarily apply to other combinations of oil and paper.

5.2.2 Acids

The hydrolysis of paper produces acids. The mechanisms are fairly well understood from the study of model compounds [55, 56]. The initial hydrolysis reaction causes scission of the cellulose chain. Dehydration reactions follow, where 5-hydroxymethyl-2-furfuraldehyde is a major product. This substance readily decomposes into levulinic acid and formic acid. It should be noted that these acids also undergo further reactions. Levulinic acid may form an acidic polymeric compound (known as “caramel”) while formic acid may decompose into carbon monoxide and water.

Oxidation also produces acids. There may be free acids formed (e.g. small carboxylic acids), as well as acidic groups attached to the cellulose molecular chain. Some of the latter are present in the cellulose already in new paper and board.

Obviously the oxidation of paper (as well as oil) is associated with the presence of oxygen. The higher the oxygen content the higher the rate of oxidation. In the absence of oxygen the oxidation rate will be insignificant. Reducing the O_2 content will reduce the oxidation rate but not necessarily in direct proportion to the change of O_2 content. However, as already pointed out, acids can be formed by other routes than oxidation, especially hydrolysis.

Many of these acids will have a low molecular weight thus being volatile and having a low boiling point. They will also have a high polarity, meaning that they will be hydrophilic, tending to dissolve well in paper.

5.2.3 Furanic compounds

“Furanic compounds” refers to a whole family of compounds, all of which could be described as furane derivatives. The most abundant is 2-furfural (2FAL), but 2-acetylfuran (2ACF), 5-methyl-2-furfural (5MEF), 5-hydroxymethyl-2-furfural (5HMF), and 2-furfurylalcohol (2FOL) have also been found in oil and paper. Their determination in insulating oil is described in IEC 61198.

5HMF and 2FAL are formed by dehydration reactions following hydrolysis of the cellulose and hemicellulose [55, 56]. But perhaps more important, all the furanic compounds mentioned above are also formed by oxidative pyrolysis [57].

The presence of furanic compounds is not generally considered to influence the ageing of oil or paper significantly. However, the measurement of furanic compound content, especially 2FAL, has found some use in transformer diagnostics. There is believed to be some correlation between the degree of polymerizaton of paper and 2FAL (or total furanic compound) content of the oil. This is discussed in more detail in the chapter on diagnostics.

5.2.4 Carbon oxides

CO and CO_2 are ultimate degradation products of all the constituents of paper and board. In lesser amounts also CO and CO_2 are oxidation products of the oil. The oils content of these gases is always measured in Dissolved Gas Analysis, and the production rates and relative amounts of CO_2 and CO are used in the interpretation of the results. Very high CO_2 contents from paper degradation may influence the acidity of the oil, and may thus complicate the assessment of oil condition.

5.3 IMPORTANT DEGRADATION PRODUCTS OF OIL

5.3.1 Acids and peroxides

Although this report deals primarily with the degradation of paper, acids that originate from the oxidation of oils deserve to be mentioned. There are two main reasons for this. The first one is that the acids formed from paper and from oil are partially the same compounds. The other reason is that acidic oxidation products from the oil may influence the degradation rate of paper. Part of the acidity of aged paper is due to absorption of acids that are the product of oil degradation. Other polar oxidation products such as alcohols, aldehydes and ketones may also be partially absorbed.

A multitude of different acids can be formed when oil is oxidized. Mineral insulating oil contains many thousands of different molecules that are susceptible to oxidation, and (at least in theory) the number of different acids that can be formed is even larger. They will include both carboxylic acids and phenols, and range from the simplest possible representatives from both groups to very large and complex molecules. Likewise they will represent a very wide range of acid strength. However, it has been demonstrated that the strongest and most polar acids, such as low molecular weight carboxylic acids, are those that will have the greatest influence on paper degradation [47].

Some observations from oxidation stability testing of oil may be interest in this context. The most widely used test method for mineral insulating oil is IEC 61125, method C. In this test air is bubbled through the oil under test. Any volatile acids formed are carried with the air flow and trapped in an absorption vessel containing water. The amount of acids in the water, as well as that remaining in the oil, is determined. The proportions may vary widely, but usually the amounts of soluble acids (left in the oil) and volatile acids (trapped in the water) are of the same magnitude. Thus, a substantial proportion of the acids produced by oil oxidation can be assumed to affect the ageing of cellulosic insulation.

While acids are formed in a relatively late stage in the oxidation process, and significant amounts of sludge even later, peroxides are among the first oxidation products to appear. They are very reactive and a key intermediate in the oxidation process of paper as well as oil.

Both acids and peroxides will help mobilize metals (in particular copper) which can act as catalysts in the oxidation process. Metals can be dissolved as salts (soaps) with acids or peroxides, but there are surely a wide range of different complexing agents present in mineral oil that assist in the solubilization of metals.

In inhibited oils, *i.e.* oil that contains a synthetic antioxidant such as DBPC (ditertbutylparacresol, sometimes called BHT - butylated hydroxytoluene), the production of acids and peroxides is very low as long as there is sufficient inhibitor left in the oil.

5.3.2 Sludge

Sludge consists of degradation products that have low solubility in the oil. Sludge may be present in the form of suspended particles, or as deposits. Most of the sludge is due to oxidation of the oil, but degradation products from other materials (including paper) most likely contribute to the total amount. The low solubility of sludge is due to the high polarity, and possibly to some degree to a high molecular weight, since some degradation products may polymerize.

There are analysis methods for the determination of sludge in transformer oil, i.e. in IEC 60422. Note that the amount of “sludge” determined by such a method may include not only sludge already present as a solid, but also sludge that is precipitated when the oil is diluted with a nonpolar solvent (such as heptane). This could be seen as a kind of “potential” sludge. A rise in oil acidity can also be used as an early warning of sludge formation. For evaluation of the hazardous influence of sediment and sludge, as well as for estimating the effectiveness of the maintenance measures, e.g. reclaiming, it is favourable to determine the type of sludge: chloroform soluble or chloroform insoluble. The presence of chloroform insoluble sludge (which is formed by further oxidation of chloroform soluble sludge and points to progressive oxidation processes) can be estimated by washing the glass filter with the sediment with chloroform (see procedure described in IEC 60422). In case of particles still present on the glass filter, chloroform insoluble sludge is present.

Large sludge deposits may be a hindrance to oil flow, and thus prevent proper cooling of all parts of the windings. Sludge is usually strongly acidic and contains peroxides, and has been shown to promote paper degradation [46]. Since sludge is mainly oxidation products of oil, preventing the oil from becoming acidic also prevents the formation of sludge. Thus, any measures taken to prolong life of the oil will also be measures against sludge formation.

Sludge can be at least partly removed by on-site treatment. One example is the use of special regenerative oils, that have higher solubility for sludge than normal transformer oil. If a transformer is temporarily filled with such oil, some of the sludge will be dissolved. Oil reclaiming has the same effect. However, especially in the latter case, the efficiency of sludge removal will depend very much on oil temperature during the treatment. The higher the temperature, the more sludge will be dissolved. Sludge present as suspended particles and “potential” sludge, *i.e.* not yet precipitated sludge, will of course be removed whatever the temperature.

5.4 OTHER DEGRADATION PRODUCTS

5.4.1 Hydrocarbons

Even though hydrocarbons in the oil, as measured in the Dissolved Gas Analysis, are usually attributed to oil degradation, some of the total amounts surely originate from paper degradation. However, this is normally not taken into account when interpreting DGA results.

5.4.2 Hydrogen

The development of hydrogen, as well as further fault gases like methane seems to be promoted by the presence of insulating paper in comparison to oil alone [58].

5.4.3 Miscellaneous

Cellulose fibres, although perhaps not a degradation product in a strict sense, may affect the safe operation of a transformer. Especially at an advanced stage of ageing, when there are large amounts of particles in combination with a high water content of the solid insulation and the oil and the dielectric breakdown voltage of the oil may be significantly lowered. However, this condition is easily corrected, at least temporarily, by reconditioning of the oil [6].

Finally there is a multitude of oil-soluble paper degradation products, which may find use in transformer diagnostics. Just like furanic compounds are beginning to be used today as ageing indicators, there may be many other compounds, whose concentrations in the oil can be measured, and that may give useful information about the condition of the solid insulation. Some of these are discussed in the chapter on diagnostics.

5.5 IEC, AND CIGRE PUBLICATIONS RELATED TO DEGRADATION PRODUCTS IN IMPREGNATED INSULATION SYSTEMS

IEC 60422	Mineral insulating oils in electrical equipment - Supervision and maintenance guidance
IEC 60296	Fluids for electrotechnical applications - Unused mineral insulating oils for transformers and switchgear
IEC 62021	Insulating liquids - Determination of acidity - Part 1: Automatic potentiometric titration
IEC 61198	Mineral insulating oils - Methods for the determination of 2-furfural and related compounds
IEC 60599	Mineral oil-impregnated electrical equipment in service - Guide to the interpretation of dissolved and free gases analysis
IEC 60666	Detection and determination of specified anti-oxidant additives in insulating oils
CIGRE	Working Group 12.18 "Life Management", Brochure N° 227, 2003

6 DIAGNOSIS

6.1 ESTABLISHED CHEMICAL DIAGNOSIS FROM OIL SAMPLES

6.1.1 Water

Water in the insulation influences the life of a transformer in many ways: Accelerating ageing, increasing losses, reducing insulation strength and introducing the risk of bubble formation during overload. To avoid premature ageing of the cellulose insulation, the equipment's water content must be kept to a minimum when it is being commissioned. However, changes in the water content during cellulose degradation are inevitable and substantial (resulting from the cellulose degradation process). A large number of studies have been conducted on the various phenomena involved in the equilibrium of water between oil and paper based on temperature. They involve the complex interpretation of the water measurement in the oil to evaluate the humidity of cellulose insulation [31,59]. The knowledge of sampling temperature and of oil state (new or aged) is important for the right evaluation of the humidity in the solid insulation.

6.1.1.1 Dependence between humidity in oil and humidity in the solid insulation.

Theoretical curves – sometimes known as Oommen curves – have been drawn, describing equilibrium conditions between new oil and solid insulation at different temperatures [10]. Application of these curves presuppose sufficient time to reach equilibrium of water between solid and liquid insulation. They are theoretically derived from two experimental curves, describing the water content concentration in paper versus relative water content in oil being in balance with that of air on one hand (Figure 24a) and water content concentration in oil versus relative water content of air – again in balance with the relative water content of air on the other hand (Figure 24b). These curves are in line with earlier direct measurement on unaged materials as shown by Fabre and Pichon [11] and Spicar (Figure 23). The temperature dependence is evident and well known. Their applicability for other liquids having different water solubility is not well studied, but it is known that water solubility depends among other factors on the aromatic constituents of an oil, so most likely the curves are less general than one likes to assume.

Equilibrium phenomena are dependent on temperature, thickness and humidity of the insulation material. The diffusion takes a long time at low temperatures and low water content contents. Practical experience shows that an equilibrium state requires more than three weeks of a steady mode of operation [60]. In fact, the diffusion time is even longer, since thick structures (e. g. laminated wood) require long times to reach equilibrium.

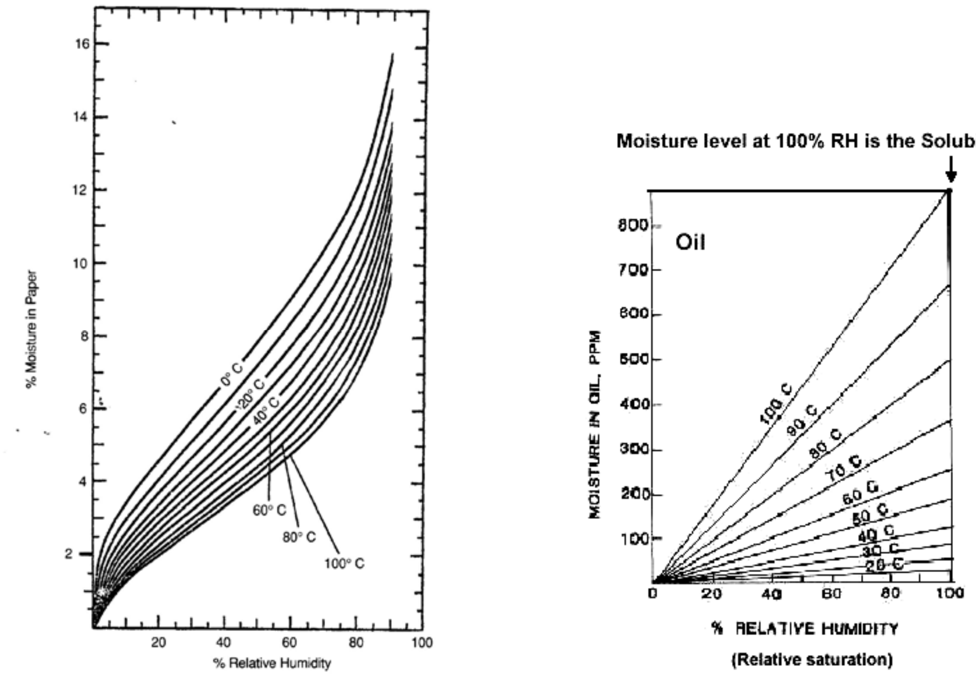

Figure 24: a) Dependence between absolute water content in paper and relative humidity [9]. b) Dependence between absolute water content in new oil and relative humidity according to [7].

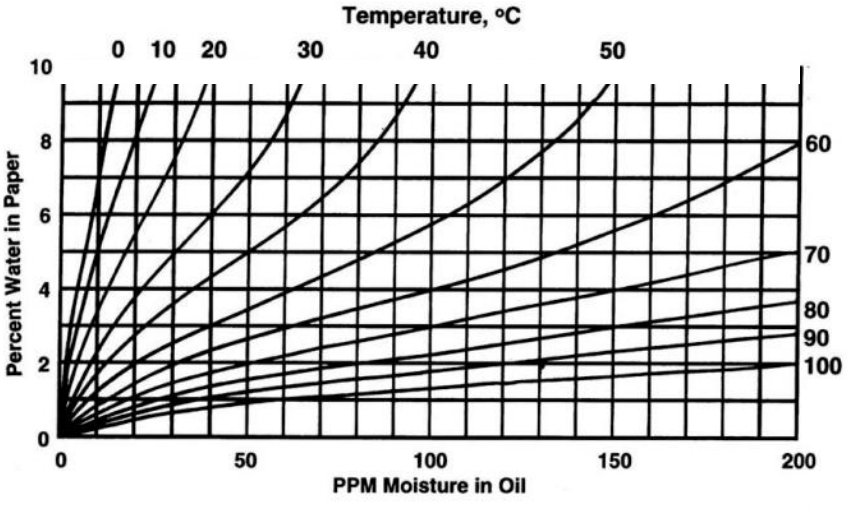

Figure 25: Oommen curves for water content distribution between new oil and paper.

However, using these curves for aged insulation systems can give large errors: Aged oils show a significant increase in the water absorbing capacity and the curve Figure 24b is strongly shifted [60, 61].

Based on that profile, the familiar equilibrium curves (Figure 26) for new oil (continuous lines) were supplemented by curves for some analysed, aged oil (dashed line). The oil was strongly aged (acidity 0,22 mg KOH/g oil and dissipation factor 3,6·10^{-3}). The error by disregarding changes in oil's water solubility due to ageing is significant: equilibrium curves for a new oil indicate water content in the solid insulation between 3 and 5% (red dots), which would indicate a wet transformer, while, by considering the equilibrium curves of aged oil, the resulting values in the solid insulation were only 1.5 – 2.2% (black circles), which were later confirmed by direct measurements on the paper.

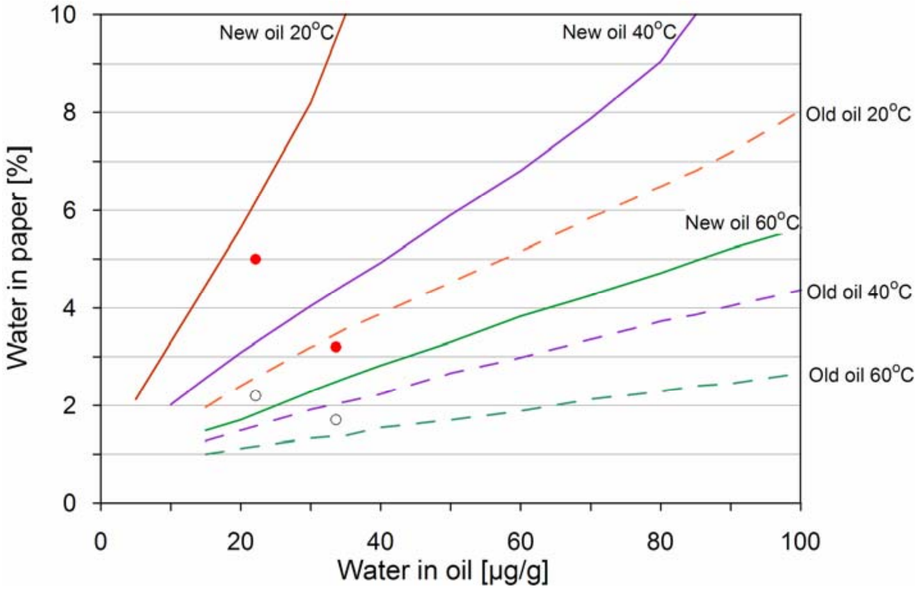

Figure 26: Water content equilibrium curves for paper in new (red dots) and aged oil (black circles). After [60].

Additionally, it is important to know the transformer temperatures during oil sampling to get a reasonably good assessment of water content in the cellulose insulation.

6.1.2 DGA

Over the last 30 years, the analysis of dissolved gases in oil (DGA) has been recommended as a good practice for detecting and characterizing incipient faults in the paper-oil insulation; see Table 3. It has been shown that the amount of dissolved carbon monoxide and carbon dioxide in oil could be correlated with the degree of polymerization and the tensile strength of the paper [62]. In 1990, Goto et al, [63] suggested a method to predict the residual life of a transformer based on the total CO and CO_2 generation. However, it should be noticed that carbon monoxide and carbon dioxide are also – normally in lesser quantities - produced by the thermal degradation of the oil, layers of paint, varnish and phenolic resins, which are used as transformer components. Carbon dioxide could also result from atmospheric contamination especially when an open, free-breathing configuration is used. Experiences have shown [64,65] that the ratios between CO_2 and CO must remain moderate (lower than 10). The IEC standard IEC 60599 [66] suggests CO_2/CO ratios above a value of 3 for normal ageing. Otherwise a fault involving excessive paper degradation can be suspected.

Recently the use of ANN (Artificial Neural Network) has been tested to model the age estimation of the paper insulation in power transformers with these by-products [67]. These two diagnostic gases can also be combined with furanic compounds analysis in oil to relate cellulosic insulation degradation state [68].

6.1.3 Furanic compounds

Several mechanisms for the thermal degradation of cellulose have been proposed, depending on whether the predominant step is pyrolysis or hydrolysis of the glucose units [33]. In the first case, pyrolysis of glucose, the reaction proceeds via levoglucosan (1,6-anhydro-β-D-glucopyranose) a dehydrated sugar which, after a series of bond rearrangements and further losses of water and formaldehyde (or hydrogen plus carbon monoxide) yields furfuraldehyde (2-furfural) among other products. The hydrolysis of glucose units proceeds through the formation of an epoxide or an enol followed by internal re-arrangements and further dehydration and elimination of formaldehyde to yield furfuraldehyde and other products. Figure 27 shows a proposed mechanism.

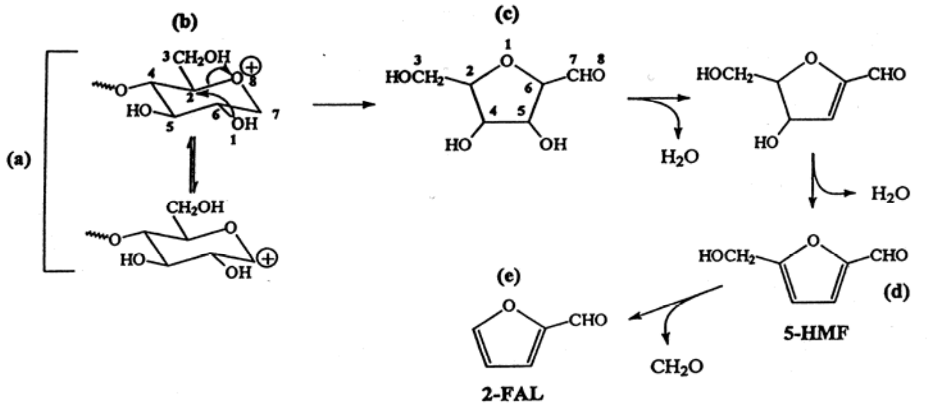

Figure 27: Cellulose degradation mechanism.

It is noteworthy that *water* and *carbon oxides* are the main by-products of the thermal degradation of cellulose. *Furanic compounds* and *carbonyl derivatives* are the second major degradation products, whereas *alcohols, acids,* and *aromatic* and *aliphatic hydrocarbons* are minor products [69].

6.1.3.1 Origin

In 1984, Burton *et al.* [70] suggested that the analysis of furanic compounds (2-furfural, 5-methyl-2-furfural, 2-furfurylalcohol, 2-acetylfuran and 5-hydroxymethyl-2-furfural) dissolved in oil could be used to characterize the thermal decomposition of the cellulose insulating paper at temperatures as low as 100°C.

Since the first work conducted by Burton, a large number of papers dealing with the analysis of furanic compounds in oil (especially 2-furfural) have been published [71,72]. Techniques that use liquid chromatography analysis [73] are most often used. Less complex and costly than gas or liquid chromatography coupled with mass spectrometry, these methods allow furanic compounds to be detected at thresholds close to the ppb range.

It has been proposed that furanic compounds may primarily originate from the degradation of hemicellulose rather than cellulose. According to several authors [59,74,75], this could decrease their potential for use given that hemicellulose is the most fragile part of the paper and that it is not really representative of insulating paper (it accounts for 10 - 20 % of the latter's composition). However, the degradation mechanisms proposed at temperatures between 100° and 200°C show that 2-furfural (2FAL) should also be generated through the 5-hydroxymethyl-2-furfural (5HMF) resulting from the cellulose. Table 3 gives the overview of the studies.

Table 3: Species already used for paper diagnosis (Oil analysis).

Molecules	**Appearance**	**Method of detection**	**References**
PAPER			
Furanic compounds	Real transformers	Liquid chromatography	Burton et al. (1984) [70]
	In the laboratory at 20,80 and 110° C		Unsworth et al. (1990) [71]
	In the laboratory 110-140°C		Shroff et al. (1985) [49]
	Lab tests and real transformers *(Cigre TF 15.01.03)*		A.De Pablo et al.(1997) [73]
CO and CO_2	In real transformers	Gas Chromatography	Yoshida et al. (1987) [62]
			Goto et al. (1990) [63]
			Dominelli (1995) [65]

6.1.3.2 Correlation with the degree of polymerization

The correlation between the paper's loss of mechanical properties, which are intrinsically linked to a decrease in its degree of polymerization and changes in some furanic compounds, mainly 2-furfural, was verified (logarithmic relation established by Shroff and Stannett [49] in 1986).

In 1996, Hill, Darveniza and Saha [76] attempted to establish a model for generating furanic compounds based exclusively on the splitting of glycosidic chains which is directly related to a decrease in the degree of polymerization. In 1999, based on research conducted by CIGRE Working Group 15.01.03 [73], De Pablo [77] developed a new degradation model. Later validated by Serena [78], the model suggests that each time three cellulose chains are broken, one 2-furfural (2FAL) molecule is generated. Correlation between DP and the furanic compounds evolution obtained in laboratory ageing tests is shown on Figure 28.

The establishment of these relationships is important for interpreting the furanic compounds but it is clear that the resulting diagnosis will depend on our knowledge of the amount of paper involved. The non-negligible effect of the water and the acidity of the oil on the formation kinetics of these compounds did not allow the authors to establish a foolproof model. The kinetics could also probably vary if the equipment involved operates in a nitrogen atmosphere or is insulated with thermally upgraded paper [79]. Shkolnik et al [80] also noted this variation and proposed a new model in 1999 exclusively for those papers.

It is now more clear that a general dependence between the 2-FAL and an average degree of polymerization of the cellulosic insulation is not likely to exist, but will be dependent on the operating conditions.

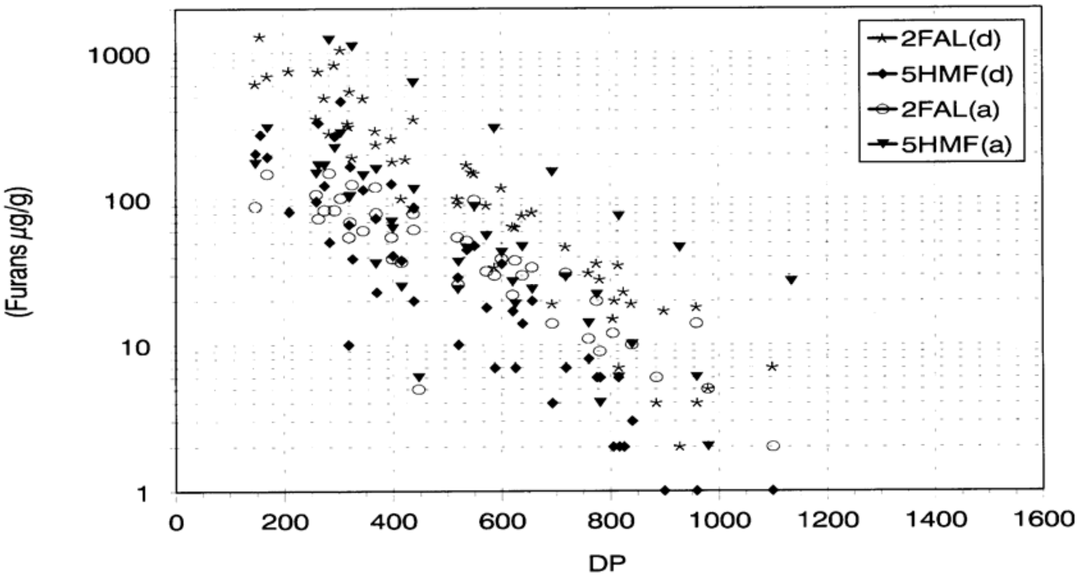

Figure 28 **:** Furanes in oil vs. DP. Collected laboratory data [73].

6.1.3.3 Critical thresholds

Although the analysis of furanic compounds combined with DGA analysis presents a certain level of reliability, it is still difficult to use their threshold values or ratios for diagnostic purposes due to a lack of knowledge of how these compounds are formed and evolve over time.

Furanic compounds evolve according to a relative rate which is always about the same, i.e. mainly 2-furfural (2FAL) (always the main compound), 5-hydroxymethyl-2-furfural (5HMF) and 5-methyl-2-furfural-2 (5MEF), followed by 2-acetylfuran (2ACF). As for 2-furfurylalcohol (2FOL), only some authors were able to note major changes in this compound which could be caused by degradations at higher temperatures [64,81], but this was not systematically noted in thermal degradation studies. Based on a CIGRE Task Force 15.01.03 study [73] where the furanic compounds absorbed on the paper had also been analyzed, 5HMF was the compound primarily found. However, it appeared to be retained to a far greater extent than 2FAL on the paper, thus making it less accessible in oil.

In general, most of the authors agree that there is a single critical threshold for equipment of about a few hundred ppb in 2-furfural. According to a US consultant company, for a representative population of U.S. transformers, 90% have less than 100 ppb of 2-furfural. In Europe, the same conclusion was reached in a statistical survey done on more than 5,000 transformers [73].

It should be noted that when European statistics are compared against North American figures, the levels of furanic compounds that are generated are greater in Europe. This fact can be related to the predominant use of thermally upgraded paper in North America since the beginning of the 80's. Paper can be thermally upgraded by impregnating it with dicyandiamide (dicy) or by other processes such as the Insuldur method. In this respect, it has been suggested [64, 82] that these molecules, which are added to the paper to increase its thermal resistance, could lead to a degradation of the furanic compounds by-products over time. Another possible hypothesis is that these compounds are not formed as easily in upgraded paper.

Finally, one should not forget that in some transformers one uses mixes of upgraded and non-upgraded paper, and in almost all transformers the pressboards are non-upgraded even if all paper is upgraded.

Even if some critical thresholds based on laboratory experiments have been proposed [83], the utilisation of those classifications are still very difficult in the field. A CIGRE statistic on transformers in service is about to be carried out. This will be the principal aim of the CIGRE TF D1.01.13 “Furans for diagnostic” which began its activities in June 2005.

6.1.3.4 Partition coefficients between oil and paper

Furanic compounds present in the impregnated insulation system are primarily found in the paper. Allan [84] proposes some partition coefficients for a few furanic compounds which would, at least in the case of 2-furfural, not be dependent on the temperature (between 25° and 90°C). For example the author suggests a ratio of 2FAL concentration in oil to the concentration in paper of about 0,2 at 25^{o}C. This ratio allows one to suppose that even after the oil is regenerated (which would eliminate its furanic compounds), the balance of the furanic compounds in the paper-oil complex would once reestablish the content in the oil, thus restoring the information concerning the condition of the cellulose insulation. The coefficients found for the other compounds at 25^{o}C (i.e. for 5HMF, 2FOL, 2ACF and 5MEF) are 0, 0.03, 0.61 and 0.49, respectively. These coefficients are more dependent on the temperature.

Myers and Sans [85] suggest that the partition of the furanic compounds between the oil and paper is affected by the oil’s rate of water saturation. According to these authors, the greater the amount of water dissolved in oil, the lesser the concentration levels of furanic compounds. Griffin [86] observed roughly the same phenomenon, and believes that the division of furanic compounds in the transformers is fairly complex even if it is not dependent on temperature. He also noted that at 200°C, a damp paper retains most of the furanic compounds it generates, which is not the case for paper heated in the same way but previously dried.

However, the furanic compounds would appear to migrate quickly in the oil; at 80°C it would appear that equilibrium is attained in less than 48 hours.

Pahlavanpour et al [87,88] also observed that the furanic compounds are more absorbed in paper than in oil. They also noted that the correlation between these specific compounds detected in oil and the DP value of the insulating paper is not easy to establish since they are depending of a lot of factors such as temperature, type of oil, type of paper, transformer design, and so on.

To refine the ageing models using the furanic compound measurements, it will be crucial to find the partitioning of furanic compound between paper and oil as well as the parameters, which could influence them. Some recent works [89,90] showed that the ratios paper/oil of furanic compounds are:

- Greatly influenced by the humidity of the paper (which is related to the water content in oil).

- Less influenced by temperature unless it is in conjunction with an acidic oil (0,16 mg KOH/ g oil).
- Different for each furanic compound (particularly between 5HMF and 2FAL).
- Also influenced by the type of paper.

As an example, the

Figure 29 shows the 2-furfural partitioning between paper and oil in different conditions.

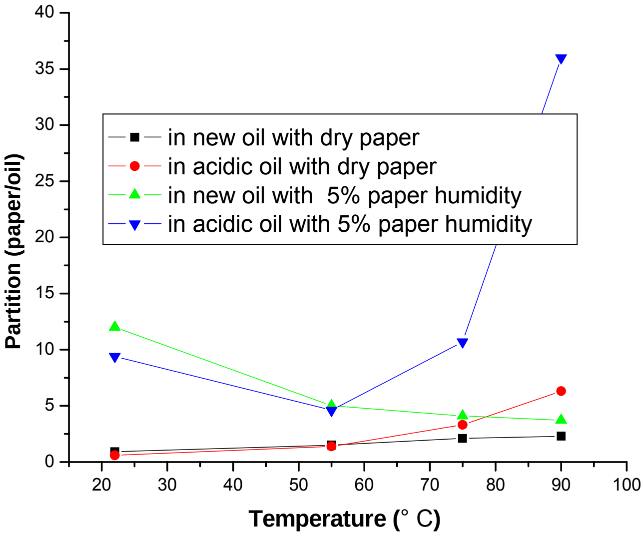

Figure 29**:** 2-Furfural partition between paper and oil versus temperature.

6.1.3.5 Stability

There is still no consensus concerning stability of the compounds above 110°C. For instance, Griffin [91] believes that the presence of water in the transformer could degrade 5HMF. Allan [84], for his part, suggests that the furanic compounds are stable at operating temperatures in the absence of any oxygen but after 8 weeks at 110°C when oxygen is present, he observed a non-negligible loss of 2-furfural (20 to 40%) and a substantial loss of the corresponding alcohol (40 to 100%). Lutke et al. [92] observed the same kind of instability in presence of oxygen, even at operating temperature as low as 60^{o}C.

In 2000, Emsley *et al.* [93] made roughly the same observations: with the exception of 2FOL, the furanic compounds are stable up to about 140°C. However, in his opinion the lack of stability of 2FOL would be an asset since its presence could only be attributed to a very recent fault. The team headed by S.D. Myers [85] even suggests that the four furanic compounds normally found at very small concentration levels than 2-furfural appear to be transient species and would not be found during a transformer's normal ageing process.

As part of another study, Emsley [31] suggests that in the case of transformers undergoing normal ageing, i.e. without any thermal faults, the presence of furanic compounds could mainly be attributed to hydrolytic degradation. This leads one to assume that at low temperatures their development could be attributed to a greater extent to the acidity or water content in the oil rather than the thermal degradation of the cellulose insulation. Scheirs

[59,75] made the same observations when he noted furanic compound levels that were much higher where water content tends to accumulate than elsewhere in transformers.

6.1.3.6 Establishing ratios between the generated compounds

Numerous authors have attempted to establish ratios between the various furanic compounds in order to determine the default temperature involved and to help determine the equipment's lifespan. In 1988, Burton [94] attempted to determine the fault temperature between 140° and 350°C by using a 2FAL/5MEF ratio. In 1990, a CIGRE working group [95] also proposed a 2FAL/5HMF ratio which would allow the fault temperature to be determined between 60° and 130°C. In 1992, Grant [96] proposed a 2FAL/2FOL ratio, while in Japan, Nanba *et al.* [97] established a relation between 2FAL and 5HMF that appeared to be highly linear. In 2001, a study by Soares *et al.* [98] showed that the 5HMF/2FAL ratio doubles between 80° and 120°C.

6.1.3.7 Limits of furanic compounds

Furanic compounds certainly give information about the paper degradation. But this is possibly all that can be stated. Years of experience show us that their evolution is dependant on test conditions or on a transformers operating condition. Recently, the effects of water, oxygen and acidity upon ageing and type of paper have been studied [41, 47,50,92,58].

Moreover, work done by Mulej et al. [99] allowed to understand why many workers find much lower concentration of 2- furfural in transformer oil samples as compared to results from laboratory ageing test for the same DP. According to them, type and quality of oil influence not only the speed of ageing and production of furanic compounds but also their quantity, stability and solubility in oil.

Lutke et al [92] even concluded that due to these limitations, it will not be possible to predict the remaining life of a transformer solely based on the content of furanic compounds.

6.2 POTENTIAL NEW CHEMICAL DIAGNOSIS FROM OIL SAMPLES

Several papers were published in the 1960s [100,101] on the use of gas chromatography for measuring compounds resulting from the thermal degradation of cellulose. These experiments allowed a large number of compounds to be identified, including levoglucosan, formaldehyde, acetaldehyde, acetone and acetic acid.

In the early 1990s, Nick Dominelli [65,72] began a wide study on the possibility of detecting new compounds, both volatile and oil-soluble, resulting from the degradation of insulating paper. Table 4 lists the compounds, which have been observed thus far in laboratories or from in-service transformers.

6.2.1 Sugars

Many studies on paper decomposition showed that levoglucosan (1,6-anhydro-ß-D-glucopyranose) plays a key role in the thermal degradation of paper. Emsley [33] showed that this compound could be a key intermediate product in the degradation of cellulose in power transformers, which could lead directly to the formation of furanic compounds.

Scheirs *et al.* [59,75] anticipated and observed the creation of monosaccharides and polysaccharides during these processes. They also proposed some mechanisms to explain the formation of 2-furfural. According to these authors, 2-furfural results mainly from the decomposition of hemicellulose and, to a lesser extent, cellulose decomposition via the formation of levoglucosan. Unfortunately, this anhydrosugar is not very soluble in oil. However, in 1998, Saiid Husain [102] was able to determine its presence in in-service transformers. The technique used involved performing an aqueous extraction followed by liquid chromatography analysis coupled with a refractive index detector. Soares *et al.* [98] also noted the presence of levoglucosan, but this time at temperatures over 250°C.

Lessard *et al.* [103,104] followed the thermal degradation of insulating paper in a laboratory ageing test by using High-Performance Ion Chromatography (HPIC) for measuring specific carbohydrates such as levoglucosan and cellobiose extracted from paper. Changes in these sugars could be linked to the loss of DP.

Vergne [74] also noted the presence of a sugar, arabinose, in the oil of an actual transformer. He gave up on the analysis since he was not able to optimize the oil extraction (aqueous extraction). The analysis of aqueous extractions of paper obtained from models aged at 100°C and 140°C allowed the detection of four sugars, i.e. arabinose, galactose, glucose and xylose. It is interesting to note that the only compounds, which Vergne was able to observe at 100°C were HMF and arabinose.

The possibility of following potentially oil-soluble carbohydrates, alcohol carbohydrates or organic acids that could be formed in the cellulose degradation process has not been ruled out. The major challenge is to find an appropriate and efficient extraction technique to detect them even in small concentrations in the oil before the furanic compounds are formed.

6.2.2 Organic acids

Koreh *et al.* [105] used liquid chromatography coupled with mass spectrometry to determine the presence of 3-furoic acid methyl ester. An interesting fact is that it seems to develop at concentration levels on par with 2-furfural. The 2- and 3-furoic acids where also identified on a few occasions [65,102].

Vergne [74] observed the development of various organic acids in oil. These consist of levulinic, formic, acetic, lactic, carbonic, glycolic and furoic acids. According to the author, the presence of the three first acids would appear to be mainly caused by the oxidation of the oil. According to Lundgaard et al. they could also be formed by reactions following hydrolysis [41,55,56].

6.2.3 Volatile compounds

Soares *et al.* [98] were able to observe in the laboratory a substantial list of volatile compounds, with the main ones being acetone, hydroxypropanone, butenal, butadione and butanone.

Acetone is another product which was observed by a few authors (Dominelli [65], Awata [106] and Keiichi [107]) both in the laboratory and in a transformer. This small volatile molecule, which is formed in negligible quantities in oil, is highly soluble in oil. In addition, Awata *et al.* were able to observe the molecule's appearance in oil well before that of 2-furfural and, what is reassuring, they were able to note a good correlation between its development over time and the paper's DP. Some authors already perceived that the molecule had excellent potential. Keiichi *et al.* developed a semi-conductor sensor capable of continuously monitoring changes in acetone.

Dominelli [65] was also able to observe the presence of various molecules of methyl sulfides where dimethyl sulphide was the major product. These molecules could originate from the residual lignin of the insulating paper sulphonated during the pulp preparation process. In this respect, these volatile and very specific molecules could prove to be significant witnesses to the cellulose degradation process.

The thesis work of Vergne [74] also helped determine the presence of methyl ethyl ketone and phenol.

6.2.4 Furanic analogous compounds

According to Dominelli [72], Wodley [101], Grant [96] and Lessard [108], the thermal degradation products of insulating papers and pressboards are not limited to the commonly studied furanic compounds. In the past few years, unknown peaks most likely resulting from species issued from paper decomposition were observed by several authors [81,109,95] in chromatograms obtained by High-Performance Liquid Chromatography (HPLC) using a reverse-phase column. The UV spectra and polarity of the compounds found indicate that they are of the furan family. However, additional work is still required to identify these peaks and to link their origin and evolution to the paper degradation.

6.2.5 Phenolic resin degradation

Phenolic resins are present in laminated wood as well as in resin impregnated paper. In 1991, Dominelli [109] observed the presence of phenolic compounds (phenol, m-cresol, o-cresol and dimethyl phenol 2,3 and 2,6 and 2,3,5, trimethyl phenol) in power transformers and linked their presence to the phenolic resins. Vergne [74] identified the same family of molecules in French transformers. These compounds could be very useful for the overall characterization of a transformer's insulation.

Table 4: Potential new markers in oil samples.

Molecules	**Appearance**	**Method of detection**	**References**
FROM PAPER AGEING			
Levoglucosane	In the laboratory at T >250°C	DSC (TVA) coupled with gas chromatography/mass spectrometry	Husain (1998) [102]
	Transformers	Aqueous extraction, liquid chromatography/ refractive index detector	Soares *et al.*(1995) [98]
Organic acids	Ageing model at 140°C and transformers	Ion chromatography	Vergne (1992) [74]
Sugars	Ageing model at 140°C	Ion chromatography	Vergne (1992) [74]
	Ageing model at 150°C	Ion chromatography	Lessard *et al.* (2003) [103,104, 108]
Acetone	In the laboratory at 120°C In the laboratory at T >250°C	$SN0_2$ sensor DSC coupled with gas chromatography/mass spectrometry	Keiichi *et al.*(1994) [107] Soares *et al.*(1995) [98]
	Japanese transformers	Not available	Awata *et al.*(1997) [106]
	In the laboratory at 150°C	Gas chromatography	Dominelli (1993) [72]
Dimethyl sulfur	Laboratory at 150°C and 160°C (pressboard and thermostabilized paper)	Gas chromatography	Dominelli (1993) [72]
Furanic analogous polar compounds	Transformers	Liquid chromatography	Burton *et al.* (1984) [70] Grant(1992) [81] Lessard (2003) [108]
Methyl ethyl ketone	Transformers	Gas chromatography coupled with mass spectrometry	Vergnes (1992)[74]
3-furoic acid methyl ester	Transformers	Liquid chromatography coupled with mass spectrometry	Koreh *et al.* (1998) [105]
FROM AGEING OF PHENOLIC RESINS			
Phenolic compounds	Transformers	Methanol extraction, HPLC/UV analysis at 215 nm	Dominelli(1991) [109]
		Gas chromatography coupled with mass spectrometry	Vergne (1992) [74]

6.3 MEASUREMENT OF THE DEGREE OF POLYMERISATION OF CELLULOSIC INSULATION

6.3.1 Context

It is possible to characterize the state of degradation of the insulating paper used in power transformers by measuring its degree of polymerisation (DP). This method is used to determine the average number of glucose units chemically linked in a cellulose molecule. During cellulose degradation, the degree of polymerization decreases from about 1200 units for new paper to as low as 150 units for paper that is highly deteriorated, brittle and friable.

The loss of mechanical strength of the paper insulation in transformers is directly caused by breaks in chains in the cellulose.

6.3.2 Sampling

6.3.2.1 Introduction

The quality and precision of the assessment related to this test primarily depends on the quality of the sampling. The DP is a localized value (only a few mg of paper are used) and can vary substantially (up to twice its value) depending on the location of the sample in the apparatus. A variation in the DP can even be observed for different layers of the sampled paper.

It is crucial to have very good knowledge of the design of the equipment involved.

6.3.2.2 Basic rules

In general, the sample taking should follow a few basic rules:

- At the winding subject to the highest thermal stress: to know the ageing state of an apparatus, the sampling can be limited to areas subject to the most potential damage.
- At the maximum local temperature: this will allow the paper that is presumably the most degraded on the winding to be characterized. For most designs, the temperature will be higher at the top of the winding than at the bottom.
- At the minimum voltage: this location must be considered if the winding is to be restored after the sample is taken (to avoid making it prone to dielectric problems).
- Reference sample: It is very important to compare the results obtained with a realistic reference. A paper sample obtained from the area that is subject to the least stress in the equipment under study will allow for a more realistic comparison than with new paper that has never been subjected to any ageing. Whenever possible, samples should be taken from a conductor that is accessible e. g. from the tertiary winding.
- Amount of paper required: To facilitate laboratory work (e.g. sample preparation, replicates), ideally 1 gram of paper is required; for instance, this corresponds to about three pieces of impregnated conductor paper roughly 20 cm in length.
- Scope of application: Since this test is intrusive (the sample is destroyed), it cannot be performed on all the transformers received at the shop. In addition, unless the equipment is being de-tanked, the windings cannot be accessed. However, samples may be taken from insulated high voltage leads accessible from inspection hatches at

the top of the transformer tank as an indication of the degree of polymerisation in a hot region of the transformer [110].
- The samples must be taken carefully; it is possible that part of the winding paper must be repaired after the sampling so that the windings are not affected.

6.3.2.3 Inspections or repairs of equipment

In case of inspections or repairs of equipment that will eventually go back in service, adequate samples are easier to obtain. A visual inspection of the windings will help in this process. Sample-taking will be limited to a minimum number of samples and should be strategic, i.e. it should be representative of the general condition of the equipment or winding involved. In fact, if the inspection shows that the cellulose insulation has obviously not considerably aged, the test should not be done. However, such a test will be very useful in specific cases where the residual lifespan of a winding is potentially at risk; should a winding be kept or replaced?

6.3.2.4 Insulating paper life monitoring

Planting of several paper samples could be done in new transformers to monitor the residual life of the insulating paper [111]. A first sample should be sent for analysis after the factory testing as an initial DP benchmark. This first DP, taken after the dry out, should be around 1000 or higher. These specific samples should be mounted and accessible from the top of the equipment (it will only need partial oil-drain, but no de-tanking). From such paper samples also the water content and the level of contamination (acids, furanic compounds, etc.) the paper will have in mutual exchange with the oil may be found. Experience has shown uncertain correlation with winding ageing due to different temperatures, put possibly the method may be used if one “corrects” for temperature differences using the earlier described formulas.

6.3.2.5 Micro-sampling of paper

The possibility of sampling a very small piece of paper (not much more than a piece of a few cm^2) from transformers in-service has also been experienced with satisfaction by a utility. This sampling which should be carried out with an accurate technique (the insulation integrity shall not be affected), combined with a furanic compounds and a dissolved gas analyses (DGA), should lead to a better insulation life assessment [110].

6.3.2.6 Post mortem inspections

When transformers to be scrapped, it takes little additional effort to gather samples of the solid insulation for the determination of its ageing condition. For a comprehensive ageing replica it is necessary to take samples systematically throughout the transformer.

- compare real ageing with laboratory accelerated ageing experiments.
- compare predicted ageing (temperature profile!) with real ageing of different solid insulation components.
- verify the cooling performance of the transformer active part.
- detect of unintended, hot spot areas, design flaws.
- identify the location of the true hot spot(s).

- count back of initial DP values of different solid insulation components (when the transformer was put in service).
- assessment of the condition of similar transformers still in operation.

6.3.3 Test procedure

The determination of the degree of polymerisation shall be carried out in accordance with IEC 60450. For a well-performed DP measurement repeatability would typically be 2 % and reproducibility will be about 10 % [112].

The viscosity of a solution of macromolecules is dependent on the molecular weight at a given (low) concentration. This phenomenon is used for the determination of the DP of cellulosic insulating materials.

A small amount of deoiled and fluffed paper or board (50 to 100 mg) is dissolved in Cupriethylenediamine (Cuen). The viscosity of the paper solution is determined using a capillary viscosimeter. From this result the degree of polymerization is calculated using experimentally established equations and constants that can be found in the relevant standard.

6.3.4 Results from post mortem analysis

In the years 2003 to 2005 post mortem inspections were made on three power transformers taken out of service [113]. On the example of one of these units the interesting and partly unexpected findings shall be illustrated:

- Voltage:	380 / 220 kV
- Phases:	1
- Rating:	600/3 MVA
- Cooling:	OFAF
- In service:	1962 - 2005

The single-phase unit consisted of two wound main limps and two side limps. The tap winding was in a separate tank. HV and LV winding were disk type, tertiary winding was helical type. All the solid insulation was made of pressboard, hot press dried for cylinders, spacers and washers, laminated for strips and spacing blocks and low density for moulded parts such as angle rings and caps. All the material surfaces were in very good condition and did not show traces of ageing. It was possible to take as many as 300 samples, 169 of which have been analyzed. In Table 5, the measured DP values are summarized.

Table 5: Measured DP values from the insulation of a 600 MVA transformer that has been in service for more than 40 years.

Insulation			Bottom	Middle	Top
End	LV	Angle ring	882-1089		
	HV	Angle ring	482-973		488-912
		Spacer			620-753
Inter winding	LV/Tertiary	Cylinder	713-917	724-1000	676-824
		Strip	886-1169	795-1083	791-1063
	HV/LV	Cylinder	841-1082	818-1083	613-975
		Strip	724-1182	659-1067	765-935
	HV/HV next limp	Cylinder	853	811-820	758
		Strip	811	735-995	731
Winding	Tertiary	Paper		655-742	559-599
		Spacer		761	640-728
	LV	Paper	634-651	624-758	580-608
		Spacer	643-793	608-792	585-690
	HV	Paper	676-798	645-743	493-556
		Spacer	751-776	640-739	582-722
Lead exit	220 kV	Paper		891	
	380 kV	Paper		813-853	
Stress ring	LV	Paper	938		835
	HV	Paper	683		619

The locations and the values of the measured DPs are depicted schematically in Figure 30. The horizontal, radial DP profiles at three levels across the windings are depicted in Figure 31.

The cellulosic insulation of this transformer was in very good condition. Even the most aged parts showed a DP of 500. The highest values were found for the end insulation underneath the LV winding and the cylinders of the main gap. In summary the following statements can be made for this transformer:

- The insulation of the copper conductor is more aged than the insulation between the windings.
- The spacers in the windings are more aged than the adjacent conductor paper.
- Pressboard cylinders are less aged than the strips in physical contact.
- Strips and cylinders next to the windings are significantly less aged than in the middle of the Hi-Lo insulation.
- Hot spot at top of the high voltage winding.

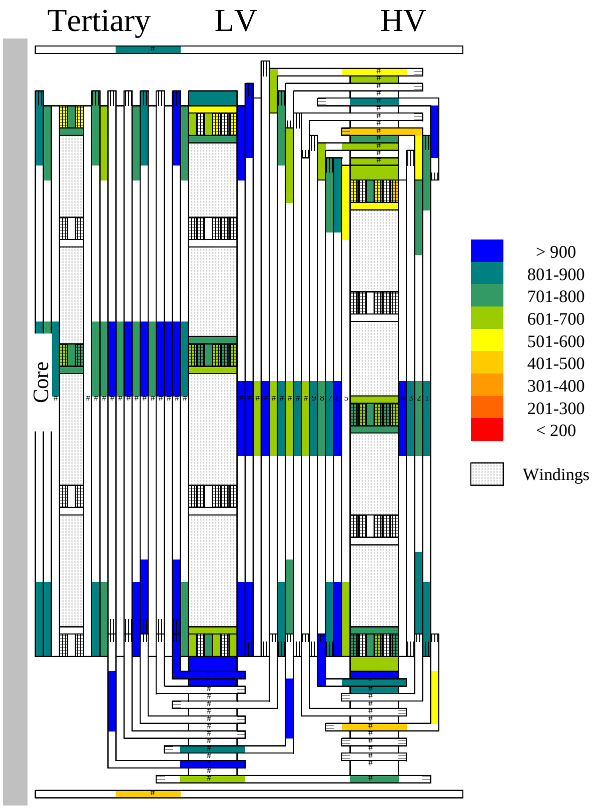

Figure 30: DP distribution, schematic, sectional view of transformer, between limbs.

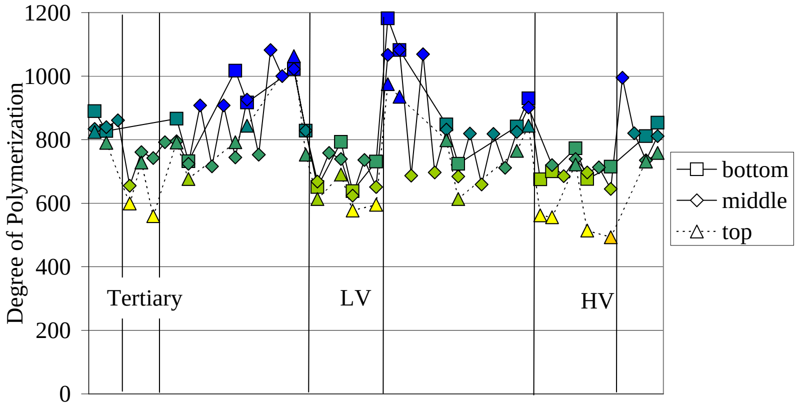

Figure 31: Radial DP profiles of transformer, between limbs.

6.4 DIELECTRIC DIAGNOSIS OF SOLID INSULATION

Dielectric measurements are standard methods for assessing the condition of a transformer or of the oil. Insulation power factor (IPF) or the equivalent measurement of tan δ is performed at ac power frequency. If these values are too high it is an indication that the insulation system is contaminated [114]. The polarization index (PI) is the ratio of the insulation resistance measure after 10 minutes to the dielectric resistance measured after 1 minute using a dc voltage; this is used for the same purpose. A PI below 2 indicates insulation deterioration.

Lately, the so-called dielectric response methods have got a considerable attention as a possible diagnostic method [115,116,117,118]. Simply put, this is measurement of the complex impedance or admittance of the transformer insulation in e.g. the main gap between the high voltage and low voltage winding over a wide (and low) frequency range (e.g. 10^{-3} Hz to 10^{3} Hz). Tan δ (or IPF) at power frequency is then only one point at these curves. The dielectric response can be measured in several ways [119]:

- Measurement of polarization and depolarization currents after application of stepped DC voltages, called polarization and depolarization current measurement (PDC)
- Measurement of currents and phase sag using a swept frequency sinus voltage, from which capacitance and tan δ can be calculated. This is called frequency domain spectroscopy (FDS).
- Measuring the voltage increase on an ungrounded transformer after it has been polarized for a certain time; the so-called return voltage measurement (RVM).

One can - with certain restrictions – by calculation transpose results from one to the other measuring method (e.g. Fourier transformation). The insulation is considered as a capacitance with oil, paper and pressboard in series and parallel. All methods depict how the full windings behave; e.g. results are influenced by the average condition and it is therefore impossible to distinguish behaviour from the upper and lower part of the winding. The measurements are influence both by the oil and the solid, and interfacial polarization (Maxwell-Wagner effects) is important. Gäfvert has described this in detail, together with the importance of the geometry and design of the winding [120]. Cigré TF 15.01.09 showed in their work how the response of a transformer was influenced by the conductivity of the oil, and that this had confused the conclusions from the interpretation rules as given for the RVM-method [119].

It is possible to separate the influence of the oil and the solid in a response measurement. The oil has a frequency independent permittivity and a conductivity that depends on composition, contamination and temperature. The conductivity can either be measured directly (IEC 61620 - Determination of the dielectric dissipation factor by measurement of the conductance and capacitance) or read out from response measurements at either short times in the time domain measurement or high frequencies in the frequency domain measurement. The response of the solid is found for the longer relaxation times in a time domain measurement and for the lower frequencies in the frequency domain measurements. Jonscher describes response measurement and analyses for dielectric materials generally and in detail also on granular and fibrous materials in his two books [121, 122]. From response measurements at different temperatures one can design a response master curve for a pressboard [115]. This master-curve varies with water content, and promising techniques for revealing the water content of cellulose from response measurement are proposed [120, 119].

One hopes to establish similar techniques for revealing the *ageing condition* of paper and pressboard as those proposed for its humidity. However, the techniques here are not even in their infancy. Oil impregnated pressboard is in many ways similar to the transformer windings; it consist of multiple interfaces between cellulose fibres with oil in the open spaces between. The permittivity and conductivity will be influenced by acids, and polar substances formed by the ageing of the cellulose. How and if the impact of the ageing substances bound to the paper fibres and dissolved in oil are separable from the influence of water only is an open question. Here one should not forget that there exist different qualities of paper and board. For example should the conductivity of aqueous solutions from cellulose vary, then the inherent response may vary between paper or board types.

Recent results from laboratory ageing of kraft paper indicate that the effect of ageing on the frequency domain dielectric response is much smaller than the effects of water content [123].

7 LIFE MANAGEMENT OF TRANSFORMERS

7.1 MAIN QUESTIONS REGARDING CELLULOSE INSULATION

We have thus far treated the ageing of cellulose insulation in transformers and the possibilities of monitoring the condition by various diagnostic methods. The next question follows quite naturally: how can the degradation be avoided or reduced? Of course reducing temperatures by good design and cooling, and use of good materials to get a better performance is important. This however, is a question relating to specifications and designs of the full transformer and to a large degree outside our scope. We are here mainly concerned with the performance of cellulose insulation itself in the chemical environment of the transformer. Given this as a restriction, we can limit ourselves with the following questions:

- How can ageing accelerating substances in the materials of the transformer be avoided?
- How can one avoid occurrence of ageing accelerating substances in the transformer during service?
- How can ageing accelerating substances be removed from a transformer, and when in the transformers life cycle is that a profitable project?

Mainly three factors; design and materials, contaminants in the insulation system and operational conditions, will determine the ageing of a transformer. For the solid insulation – paper and pressboard - it means a combination of mechanical and dielectric performance, which are interlinked and synergetic. The mechanical performance of cellulosic insulation is given in terms of mechanical strength (e.g. tensile index) or degree of polymerisation, which are strongly influenced by ageing.

Paper ages more quickly under the influence of water and low molecular acids increasing hydrolysis, and from oxygen, free radicals and metal ions formed under reactions with free radicals (Fe^{++}, etc) contributing to oxidation. Consequently, these substances should be extracted or their formation should be prevented in order to reduce ageing.

7.2 REMAINING LIFE ESTIMATION

If the present condition of the insulation system and the operational conditions of the transformer is known this allows for a rough estimation of life expectation. Such estimation should be based on the hotspot temperature of the transformer, known from design criteria and load conditions. The critical parameter is believed to be the mechanical strength of the paper. Once the paper cannot withstand the shear stresses in the winding during a high through current transient (e.g. short circuit), the conductors will move. If breakdown does not immediately occur, a change in the geometry will increase future stresses and increase possibilities for further development of the defect. Short circuit stresses occur during lightning strokes, breakdown of nearby equipment, from unintentional energizing with earth apparatus connected, and from connecting generators in phase opposition. Frequent large inrush currents may also play a role. The magnitude and frequency of short circuit stresses must be considered when analyzing the need for scrapping a transformer. A transformer in a cable network does for example experience fewer short circuits than a transformer connected to overhead lines with frequent lightning strokes.

Two schemes for assessing ageing are possible:

- Prediction of reduced mechanical strength using equations for strength development [12].
- Testing or prediction - based on algorithms for ageing kinetics - of DP-value in paper and correlating that to tensile strength.

In any case it is the responsibility of the transformer owner to choose a criterion for end of life. Often a DP value of 200 is recommended, a value that according to the figure shown below will indicate a 30% remaining tensile strength.

According to IEC loading guide, that to a large degree is based on Montsingers work [14], ageing rate doubles (or life is halved) by every 6-8 ^{o}C temperature increase. This essentially describes an Arrhenius relation where T is the absolute temperature. In the loading guide this is simplified and expressed as a relation with temperature valid within 80-140^{o}C

$$\textbf{\textit{Rate of ageing}} = \textbf{\textit{constant}} \times \textbf{\textit{e}}^{p\theta}$$

where p describes how sensitive the ageing is to temperature, which in the IEC standard is expected to be a doubling for every 6^{o}C, and θ is the hotspot temperature of the transformer in degrees Celsius. The *Constant* describes the influence of the environment on the change in functionality (e.g. tensile strength) and is usually ignored.

The base of all this is a definition of a material test where the criterion is that paper aged under a certain condition (e.g. T_{Hot} = 98^{o}C) should not loose more than a certain percentage of its property within the period. This scheme is used for design and for material testing before manufacturing. The disadvantage for service aged transformers is that it is difficult to take samples that are suited for checking tensile strength from a service aged transformer.

Figure 32 shows how tensile strength of kraft paper is reduced with degradation of the cellulose polymer chain.

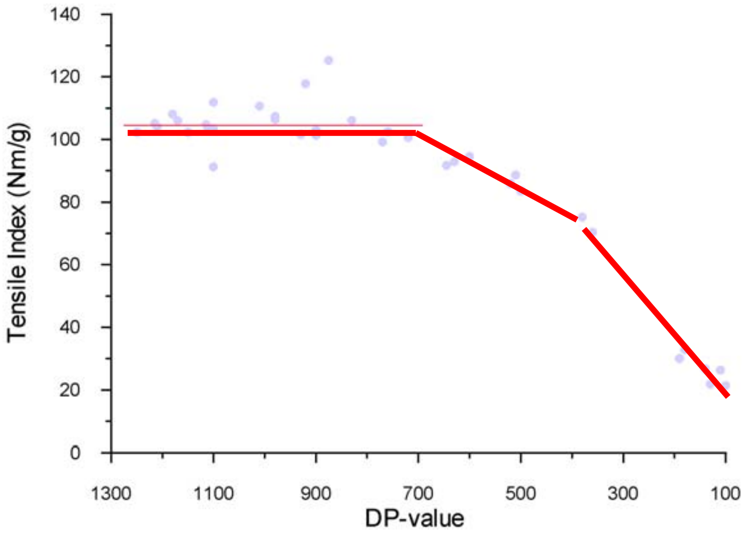

Figure 32: Correlation between tensile index and DP-value for non-upgraded kraft paper. Based on results from [41].

The chemical degradation of the cellulose can – as explained above - with some confidence be described by Ekenstams and Emsleys formulae (see chapter 3.3):

$$Expected\ Life = \frac{\frac{1}{DP_t} - \frac{1}{DP_0}}{A * 24 * 365} * e^{\frac{E}{RT}} \left[year\right]$$

DP_0 is in the range 1000 – 1250 and DP_t is defined by the user from his preferred margin of safety for the transformer. *E* is the activation energy, *R* the molar gas constant, *T* the hotspot temperature and *A* an environmental coefficient as explained above.

One can in principle assess ageing progress by sampling as one may get valid samples from transformers after opening. However, a major uncertainty lies in how to link ageing at an accessible location to that of the critical hotspot region. One may with some confidence assume similar E and A values in the full winding, or adjust the A value for expected deviations in water content. For this one would need temperature models for the transformers. Again one should realize that expected low DP of insulating paper will seldom be the only reason for taking a transformer out of service.

7.3 NEW TRANSFORMERS

7.3.1 Quality of materials.

The most materials used in the transformer manufacturing are “traditional” materials, used for decades. The low content of conductive contaminants in the insulating material is very important and specified in numerous IEC standards. The factory drying (e.g. down to 0,3 - 0,5%) has the goal of removing water and low molecular acids from paper, pressboard, laminated wood, thus providing a high dielectric strength.

The insulating oil should – as detailed in chapter 5 - be stable against oxidation as well as against corrosion. Oxidation of oil produces peroxides and water soluble acids which as polar substances are selectively bound to cellulose, thus contributing to its degradation. Cellulose can be oxidized directly: through air dissolved in oil or through oxidation products in the oil – free radicals and peroxides. Also bare metal surfaces will contribute to formation of free radicals, and take part in ageing. Therefore metal passivators may be used to prevent this effect. The oil degradation products are of polar nature and may further deteriorate into carboxylic acids. Some information about the types of acids formed is available from standardized oxidation tests of oils, where high molecular weight acids are measured in the oil and low molecular weight acids are measured in the water trap on the exhaust of the ageing cell. Furthermore the oils tendency to form sludge may influence the cellulose through reduction of cooling and also chemically.

Choosing either kraft or thermally upgraded paper will of course influence ageing rates. As earlier explained, upgraded paper is less sensitive to acid catalyzed hydrolysis, but about equally susceptible to oxidation as kraft paper is.

7.3.2 Transformer design

The most important choice is probably the operating temperature of the insulation system, which normally is decided from a criterion of normal life expectancy under nominal conditions and hot spot temperatures of either 98 °C for normal paper and 110 °C for upgraded paper. In principle this is based on a criterion for a reduction in tensile strength of not more than 50 % over the transformer life. Using upgraded paper with a 98 °C hotspot temperature would give an increased life expectancy. This criterion is probably far too conservative as many transformers operate well with far lower strength of the paper as discussed in the IEEE loading guide [13]. These considerations are valid for design and are based on ageing tests of paper under dry and oxygen free condition. In service, conditions can be far worse and an accelerated ageing must be expected with increased water content, oxygen and degradation by-products content.

Next to design and materials, the choice of protection from ingress of ageing accelerating substances like water and oxygen will determine the progress of ageing of the transformer. In the US and many other countries most of the transformers are delivered with a sealing system based either on a nitrogen cushion or a rubber bellow in the expansion tank. This will prevent ingress of water and oxygen, but also keep any water and easily evaporable acids inside the transformer.

In Europe, many transformers are open breathing, with silica gel water absorbers at the breathing inlet of the expansion tank. To have well dimensioned absorbers is vital. With open breathing systems equipped with such absorbers one may expect that some of the water formed in the insulation will be absorbed by the silica gel. However, experience shows that some European transformers may become quite wet (3-4%) so this effect cannot be very significant. Possibly water content loss from the insulation will depend on the operating temperature. Furthermore, the maintenance of the dehumidifiers is essential, especially at transformers working with a variable load, thus actively “breathing”.

Strongly oxidized oil can also represent a source of humidity, especially at higher operating temperatures.

An open breathing transformer will operate with an insulation in balance with the gasses in the atmosphere and an oxygen concentration up to 30 000 ppm in the oil is normal. The correlation between ageing rate and oxygen concentration has not been extensively investigated, but Lampe’s study [124] suggests that one needs to reduce the oxygen content from around 30 000 ppm down to below 2000 ppm to significantly reduce the effect of oxidation of a transformer, contrary to oxidation being linearly dependent on the oxygen concentration as often assumed.

7.3.3 Condition control

Here we describe some common on-line methods for extracting water, oxygen and acids out of the transformer.

Partial degassing

Small vacuum pumps for continuous use in an oil circulation circuit are commercially available. This technique mainly aims at a deoxygenation of the transformer oil and cellulose. Which efficiency is needed to arrive at a certain concentration of e.g. oxygen depends on the size of the transformer, and whether or not it is open to surrounding air. Additionally they will remove some water. For humidity control, such pumps may be debatable; they are not very efficient (efficiency again depends on the temperature of the oil and the water vapour pressure in the degassing unit), but may over time help keeping generated water content away from cellulose. There is also a possibility that volatile acids may be extracted from the oil. However, continuous degassing, may interfere with DGA analysis, reduce its sensitivity or change the basis for its interpretation.

Cold traps
To keep water content down, cold traps connected to the conservator tank are being used.

Molecular sieves or cellulosic absorbents
Traps in the oil circulation path can be used to extract water content selectively [125,126]. These can either be molecular sieves or tanks with pressboard kept at a reduced temperature. Molecular sieves can absorb water irreversibly. Since they have a potential catalytic activity, it will be important to investigate the compatibility with oil, particularly at elevated temperatures, as well as their influence on DGA. In case of cellulosic absorbers, the influence on the diagnostic parameters, e.g. furanic compound must be considered. Also, their capacity depends on the weight of absorber material, and regular replacement is necessary.

7.4 TREATMENT OF SERVICE AGED TRANSFORMERS

7.4.1 General

Here we will consider any action that singularly, periodically or continuously is introduced to slow down the ageing processes of the cellulose insulation in a transformer and extend its service life. The actions that will have an impact on the ageing can be split into three categories:

- Reduction in service temperatures that will reduce ageing according to the influence temperatures have on the kinetic processes as discussed above. This will influence ageing of both oil and cellulose.
- Oil maintenance [6] can be grouped under periodic actions like degassing, reconditioning (removal of particles and water content), reclaiming (removal of substances from ageing of oil and cellulose) by chemical absorption and finally replacement of the oil. These processes may also improve the condition of the cellulose.
- Cellulose maintenance by reducing ageing accelerating contaminants from the cellulose. Normally this involves factory or on-site drying processes like vapour phase drying, hot-oil spray, winding heating, vacuum treatment promoting evaporation and transport of e.g. water and low molecular weight acids.

The efficiency and benefit of a condition management or maintenance technique will depend on the extent of ageing of the transformer and the possibility for this technique to improve the condition of the cellulose insulation and thereby retard the ageing.

For a new transformer in good condition one can retard ageing by keeping oxygen away from the oil and paper by e.g. rubber bellows and degassers to avoid oxidation or by keeping the water concentration in the paper low by dehumidifiers as described above. If the ageing rate is kept low, the need for future actions like oil reclaiming or drying of windings will occur later.

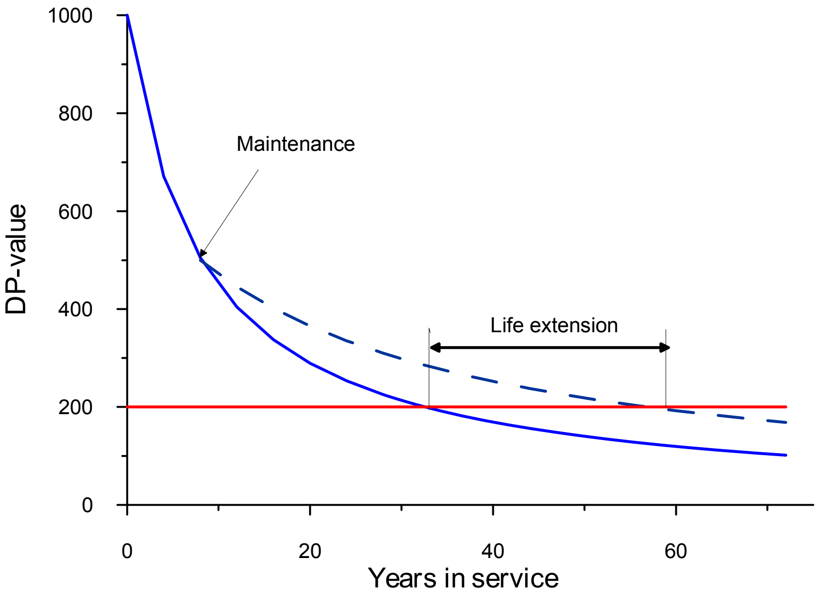

Figure 33: Simulation of maintenance action of cellulosic insulation and its effect on retarding ageing.

If the transformer has a significant water and acid content, drying and oil reclaiming may retard ageing of the solid insulation. The benefit of such actions presupposes that the state of ageing is not too advanced to get a significant life extension as is sketched in Figure 33. Looking at the mechanical strength vs. DP value of kraft paper, shown in Figure 32, where the mechanical strength of the cellulose is almost unchanged down to a DP-value of 500-600, the transformer conditions can be roughly divided into three groups:

- “New” units having a DP of around 900, water content around 0,5 %, and negligible content of water soluble, low molecular weight acids.
- Units with DP’s in the 900 to 350 range, having a moderate content of water content and acids.
- Aged units with a DP lower than 350, usually with high acidity and water content.

The cost-benefit of any maintenance action will depend both on the efficiency of the process and the extent of ageing and contamination of the transformer.

7.4.2 Transport (diffusion) of contaminants

Most maintenance and condition control techniques address either how to avoid oxygen, water and active acids being formed and/or getting into the cellulose insulation, or how to remove this contamination from the cellulose insulation once there. To assess the efficiency of certain equipment for maintenance one has to consider vapour pressures of the contaminants (water or acids) and diffusion of these out through paper, pressboard and cellulose in relation to the performance of the equipment and the duration of application. The concentrations are not homogeneous; water concentration is highest in low temperature regions; here the diffusion is lowest and it is most difficult to remove it.

When the transformer insulation is heated, the water (and probably also most other polar ageing by-products) moves from the paper to the surrounding oil/air, because water solubility of oil increases as shown in Figure 23. This is the basis for procedures for drying of the paper insulation. Next, the water transport must be made as efficient as possible; both for the diffusion of water from the inner layers of the insulation to its surface, and for the transport of the water from the surface of the cellulose to the drying apparatus. Diffusion processes increase with temperature. Therefore, high temperatures are advantageous to increase efficiency of any maintenance process on the cellulose insulation, as shown in Figure 34. Diffusion is described by Fick's law invoking a material dependent diffusion constant. However, in the case of transformers one should note that the basic form of Fick´s law may not fully describe the diffusion process. The diffusion coefficient D depends on the water content concentration [127].

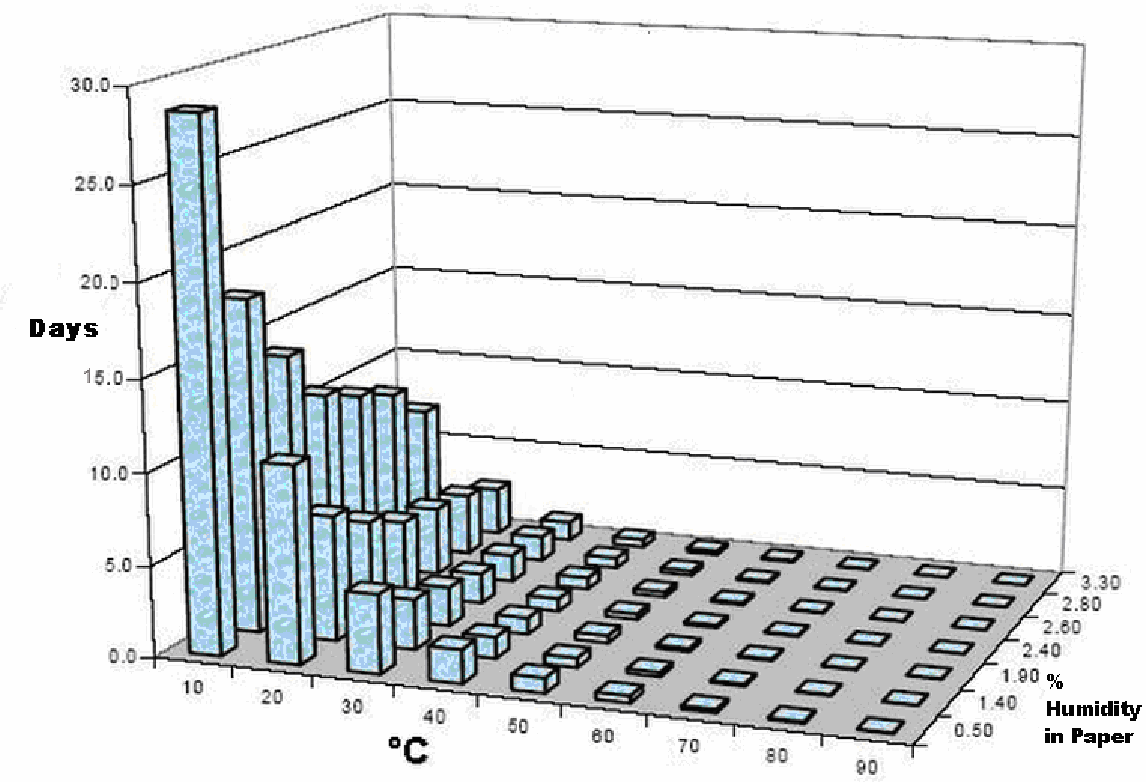

Figure 34: Sketch of time to get close to equilibrium for pressboard with type B.3.1 (EN 60641-3-1) thickness 1 mm, showing the higher the humidity in paper and/or the higher the temperature is, the quicker is the establishment of an equilibrium between insulation and oil [128].

7.4.3 Removal of contaminants from cellulose

The possibility for removing any substance from the cellulose will depend on the extraction efficiency in the surroundings of the cellulose (oil, air or vacuum). This will mainly be governed by three factors.

- The partition coefficient between paper and e.g. oil for gasses, water and low molecular acids.
- The vapour pressure of substances like water and acids at the process temperature.
- Chemical bonding between contaminants and cellulose.

The partition coefficient of water is fairly well understood (see 6.1.1.1), and techniques for removing water from the solid insulation are described extensively in Cigré Brochure No 227

[54]. However as low molecular acids are not treated specifically it is useful to give them some attention here. These acids will behave similarly to water and mainly stick to the cellulose [129]. There seems to be a synergetic dependence between solubility of water and low molecular weight acids in the oil.

While the lowest molecular weight acids have a boiling point close to that of water, the boiling temperature increases with the weight as indicated in Table 6. In reality it is the vapour pressure at the actual temperature that is relevant. A low boiling point indicates a high vapour pressure. So heating the transformer will help by increasing the vapour pressure of the water and acids, but efficiency may be low for some substances. There also is a possibility that the acids will bind to the cellulose and that this will bind water even firmer to the cellulose.

Table 6: Molecular weight, boiling point and vapour pressure of some organic acids.

Acid Type	M_r (g/mol)	T_{boil} (°C) at 1 bar	Vapour pressure	
			P [mm Hg]	Ref temp [°C]
Formic	46	101	44,8	20
Acetic	60	118	11,4	20
Levulinic	116	243	1	102
Naphtenic	285	233-375	$1{,}1 \cdot 10^{-7}$ - $1{,}4 \cdot 10^{-5}$	20

7.5 EFFECT OF OIL TREATMENT ON CELLULOSE AGEING

7.5.1 Role and characteristics of the oil

Good transformer oil should provide electric insulation and cooling of the windings, and be chemically stable. Important characteristics of the oil are the thermal oxidation stability and corrosivity. During ageing oil should produce little sludge and low molecular acids. The stability will depend on its chemical composition. Practice varies regarding using additives like oxidation inhibitors or not. Oils where inhibitors are used may be refined differently to uninhibited oils: less of the natural inhibitors (mostly polyaromatics and sulphur compounds) in the oil itself are kept. The inhibiting substances - acting as radical scavengers - are consumed by oxidation, delaying the oxidation of the oil itself. Once these substances are used the oxidation of the oil itself starts and the content of aldehydes, ketones and carboxylic acids rapidly increases. It is advisable to reinhibit the oil once the content of inhibitor has fallen to a low level (e.g. 30 % of new value) to avoid the oil becoming acidic and increasing the need for extensive reclaiming.

Acids do influence the paper ageing. It is not well known what types of acids are formed from the oil, but at least some of them are easily water soluble. Today oil acidity is measured as a sum of all acids and expressed as the total acid number. Information about the ratio between the easily evaporable low molecular weight acids and the less evaporable high molecular weight acids can be found from the oxidation stability tests [130]. However, in a transformer we expect that it is the paper ageing that is the main source of low molecular weight acids.

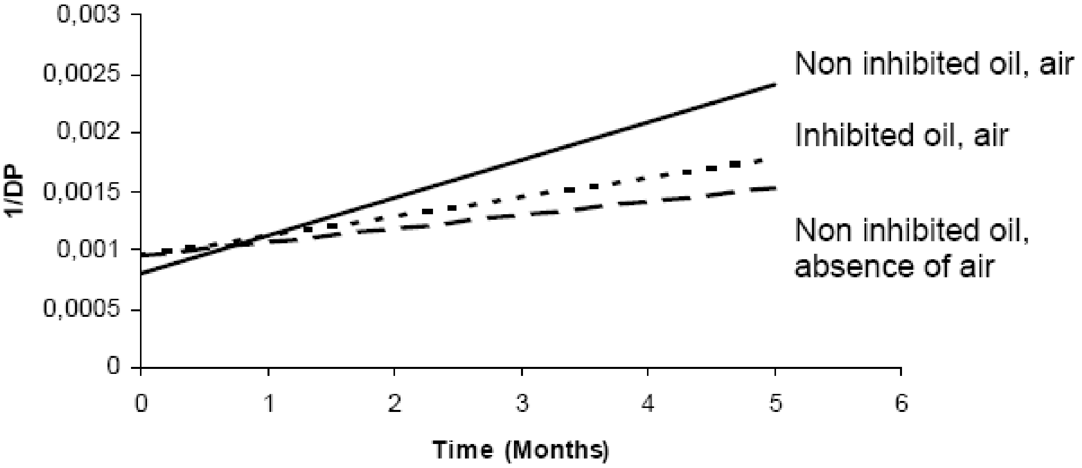

Figure 35: Progress of ageing rate (1/DP); effect of air and inhibitor at 85°C [58]. Experiment on pressboard/authentic oil with weight ratio of 1:10.

It is not known whether oxidation inhibitors added to the oil may influence the paper ageing, although it is reasonable to expect that they should have at least some effect on the oxidation rate, as found in an experiment by Kachler et al. shown in Figure 35. However, Shroff in his laboratory study found no support for such conclusions [49]. These effects need to be further investigated before any general advice can be given.

7.5.2 Oil reconditioning and reclamation

Oil *reclaiming* is a major restoration done mainly to increase the life of the oil in a transformer. The oil is passed through sorbent (e.g. Fullers earth) columns where acids and polar compounds from the deterioration of the oil and paper are efficiently removed. After reclaiming the oil needs to be inhibited – also in the case of previously uninhibited oil. Usually, reclaiming is combined with a *reconditioning* of the oil using filters to remove impurities and vacuum columns to degas and dry the oil. The oil has primarily been considered in this context as described in the IEC oil maintenance guide [6].

Maintenance of the oil will not extend the service life of the cellulose unless ageing accelerators like water, oxygen and acids are removed from the *cellulose*. If the oil is circulated several times through the columns, a good, long-term stability in the oil's acid number is reported [131] and also a reduction in water content in cellulose is found.

The following considerations indicate to what extent water content reductions may be expected. Table 7 shows some examples of drying times at some water contents and temperature levels for a 300 kV transformer of 80 MVA with 27 tons of oil and 5 tons of cellulose.

Table 7: Estimated relative efficiency of on-site drying of a transformer done by oil circulating through a drying column. Capacity of drying equipment: 5000 litres/hour with full removal of water at each pass [21].

Water content in cellulose	Weight water in cellulose [kg]	Weight water in oil at 20°C [kg]	Weight water in oil at 70°C [kg]	Water Concentration in oil at 20°C [mg/Litre]	Water Concentration in oil at 70°C [mg/Litre]	Water removed per hour at 20°C [kg]	Water removed per hour at 70°C [kg]	Relative time to reduce humidity by 1% at 20°C	Relative time to reduce humidity by 1% at 70°C
1%	50	0,027	0,270	0,9	9	0.0045	0,045	67	7
2%	100	0,081	0,810	2,7	27	0,0135	0,135	22	2
3%	150	0,162	1,89	5,4	63	0,027	0,315	11	1

In this model it is not considered that the oil in the transformer will be a blend of conditioned and unconditioned oil, and that the diffusion of water through the cellulose and convection of oil from paper to process equipment may slow the process. Furthermore isothermal conditions are assumed. Time is relative to time at 3% water in cellulose at 70°C

The example has relevance for the methods offered for on-site oil reconditioning or reclamation. The drying of the cellulose is a possible bonus effect from processes mainly focused on degassing, reconditioning and reclamation the oil itself. For all these methods the cellulose and pressboard are dried via the oil transported through the processing apparatus. The ability of the methods to get water and ageing by-products out of the winding will depend on, and increase with, the temperature of the insulation system in the transformer during the processing. To remove water will - as stated before - require time: temperature dependence of solubility and diffusion for water is basically known. It is easier to remove one percent water from wet insulation than from dry insulation because then the water concentration in the oil is higher and more water is brought to the process equipment. Preferably reclaiming should be done on transformers under load to keep a high temperature and thereby increasing diffusion in cellulose and keep the concentration of ageing by-products in the oil high.

Also, the higher the temperature, the more efficient is the removal of sludge. A prolonged treatment at high temperature may remove significant amounts of sludge. Removal of sludge will improve cooling and reduce ageing of the solid insulation Special regenerative oils, that have better solubility for sludge than normal insulating oil, have been developed. .

Oil processing will also remove acids from the oil. The efficiency on the cellulose will depend on the partitioning of the acids between paper and oil. One must be aware that it is easier to remove the high molecular weight acids than the low molecular weight acids, but that the normal measurement of acidity does not discriminate between the two.

Experiences from Sweden show that a reclaiming process reduced the water content in the cellulose “somewhat” from the original 3% to a level that was still above 2% [132].

The effect of oil reclaiming on both water and acidity of the solid insulation has been investigated on a 47 kV, 6 MVA transformer manufactured in 1947 prior to scrapping it [133]. The transformer got a new low voltage winding in 1969. The transformer contained 500 kg of cellulose and 10 000 litres of oil. Samples were taken of oil and of solid insulation from 1 mm pressboard barriers, and intake and star point connections. (No samples were taken from the winding as it was found to be varnished.) The transformer was processed with a reconditioning/reclaiming unit where the Fuller’s earth was regenerated each night. The winding was heated to 65°C using a low frequency heating system. A total number of 10 passes (40 hours) of the full oil volume with Fullers earth and 16 passes (64 hours) with only vacuum was applied.

The condition of the oil was improved from a neutralisation value of 0,15 mg KOH/g to 0,01 mg KOH/g. For the solid insulation a reduction of 30-40% in both water content and acidity could be seen as shown in Table 8. The acidity was measured using water extraction.

Table 8: Example of water content and neutralisation value in cellulosic insulation before and after oil reclaiming.

	Neutralisation value [mg KOH/g]			Water content [%]		
	Before	After	Reduction[%]	Before	After	Reduction[%]
LV $_{\text{outtake lead}}$	2.42	1.23	49	2.0	0.9	55
LV $_{\text{starpoint}}$	1.76	1.00	43	2.4	1.2	50
1 mm press-board barrier	2.08	1.45	30	1.6	1.1	31

One can conclude that even if reclaiming is not intended for restoring the paper insulation, the methods has an undocumented potential of also improving the conditions of the cellulose by removing some water and acids. However, the measured total acidity of the oil does not reflect the conditions of the paper where water soluble low molecular weight acids dominate.

In principle also, continuous degassing equipment can remove water content and acids. The efficiency will of course depend on the capacity of the pumps and the efficiency (pressure) of the degassing unit.

7.6 METHODS FOR CELLULOSE RECONDITIONING

By reconditioning the cellulose of a transformer one normally refers to singular actions using techniques able to remove the main portion of water from the cellulose. To get proper drying, one will usually take the transformer out of service and remove the oil. In general, draining the oil away and applying vacuum makes water transport easier than in oil, particularly when the drying can be done at elevated temperatures. In this case it will be the diffusion of the water through the paper that limits the drying. Up to now this has mainly been done in a factory, but now such services are being offered for on-site use.

Different methods for drying can be used. Some are based on techniques for drying of un-impregnated windings. For unimpregnated units one can apply temperatures in the 120°C range. For units from service one can use similar techniques after the oil is drained, or one can remove water and contaminants via circulating oil. The main methods are:
Vapour phase; A hydrocarbon liquid (kerosene) is evaporated whereafter it condenses on the insulation thereby heating it and building an azeotropic[8] mixture with the water in the cellulose. A series of pressure lowering allows the efficient extraction of water content. The water and kerosene vapours are extracted by vacuum pumps and separated.
Hot oil spray; Hot oil is sprayed onto the windings to heat the cellulose and evaporate the water, which thereafter is removed by vacuum.
Low frequency heating (LFH) is used to heat the windings and evaporate water, which is thereafter removed by vacuum. It can be combined with hot oil spray because it heats parts where the hot oil does not contact.

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[8] Mixture between water and kerosene with steady concentration ratio

Hot air – vacuum; Here both hot air blowing to heat and evaporate water, and vacuum to remove it, are used.
Liquid circulation as described in 6.5.2 can also be used to remove contaminants. One can also exchange the oil with another liquid that better dissolves water and contaminants (e.g.esters, oils with higher aromatic content) [134].

The methods above are listed according to their ability to quickly remove water from all parts – the vapour phase being the most efficient. The hot vapour used in the vapour phase techniques will condense on all cold surfaces. For hot-oil spray the oil will hit the outer insulation surfaces and be less efficient for "screened" parts [135]. One has to apply vacuum for a sufficiently long period to extract the water from the wood, the paper and the pressboard. In some processes the winding is heated by applying low frequency current during the drying process. This will definitively improve drying of the winding. How much it will help on ribs and barriers has to be verified. One should be careful not to apply too high temperatures when impregnated surfaces are in contact with air to avoid oxidation of the oil.

Figure 36 gives an example of the results from a low frequency heated vacuum drying of a 32 MVA transformer. Temperature was 100 – 110°C, vacuum in the transformer tank was 2 mbar, and the process was applied during 250 hours. When using these methods one has to have storage tanks for the oil. Thermal insulation of the transformer tank will improve the heating efficiency. Details about the processes can be found in [136].

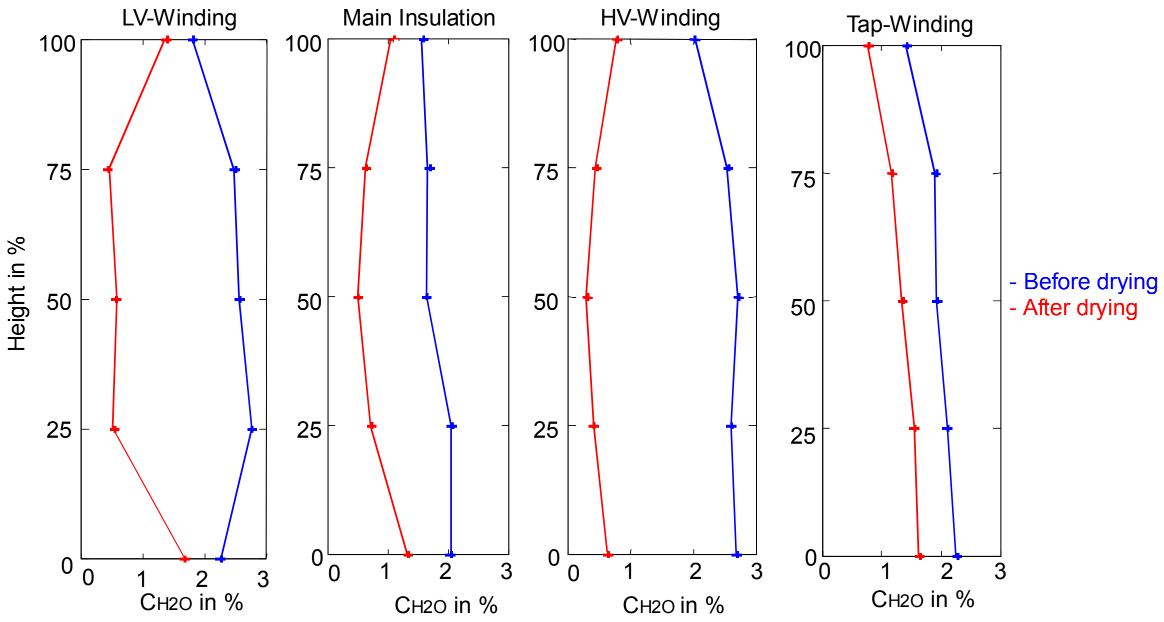


Figure 36: Water distribution in a winding arrangement before and after LFH-drying [136].

It is an open question how efficient these methods are for removing acids from the paper. We would expect that some of the low molecular carboxylic acids having a low boiling point would evaporate at the elevated temperature that is necessary for drying. This is in line with the observed high acidity of the extracted water like shown in Figure 37.

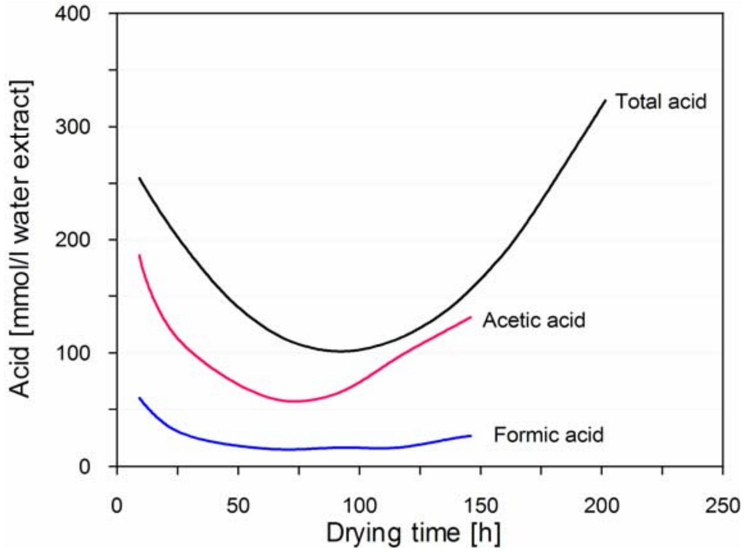


Figure 37: Extraction of low molecular organic acids during the LFH-drying [136].

Increase of water content in a transformer winding will result in swelling of the cellulose, increased clamping pressure and plastic deformation of the cellulose. After drying, the paper will shrink. Due to the plastic deformation that has occurred, a net reduction in clamping pressure can be expected with slackness in the winding as a possible consequence. For a winding, where the clamping pressure is essential to avoid displacement during short circuit stresses this has to be considered [137]. Transformer design and locally expected mechanical stresses should be considered when assessing the consequences of a possible winding slackness.

7.7 IEC AND CIGRE PUBLICATIONS RELATED TO LIFE MANAGEMENT OF TRANSFORMERS

Cigré brochure 227	“Life management techniques for power transformers”, Cigre WG A2.18 Chairman V.Sokolov,
IEC 60422 (2005)	Mineral insulating oils in electrical equipment - Supervision and maintenance guidance

8 PROCEDURES FOR VERIFYING AGEING PERFORMANCE OF CELLULOSIC INSULATION

8.1 PROOF TESTING

Standardized tests can be found in the following national and international standards. They may be of direct or indirect interest for power transformers. Care should be taken that any accelerated test replicates service conditions. For example liquids with increased water solubility may at high temperature dry out cellulose to an unrealistic level –compared to service conditions where in almost all cases most of the water will remain in the cellulose - thereby reducing hydrolysis:

8.1.1 IEC 60216-1 to 60216-6 "Electrical insulating materials - Properties of thermal endurance"

This standard specifies the general ageing conditions and procedures to be used for deriving thermal endurance characteristics and gives guidance in using the detailed instructions and guidelines in the other parts of the standard. Simplified procedures are also given, with the conditions under which the procedures can be used. Although originally developed for use with electrical insulating materials and simple combinations of such materials, the procedures are considered to be of more general applicability and are widely used in the assessment of materials not intended for use as electrical insulation. Applying this standard, it is assumed that a practically linear relationship exists between the logarithm of the time required to cause the predetermined property change and the reciprocal of the corresponding absolute temperature (Arrhenius relationship). For the valid application of the standard, no transition, in particular no first-order transition should occur in the temperature range under study.

8.1.2 IEEE C57.100-1999 "Standard test procedure for thermal evaluation of liquid-immersed distribution and power transformers"

A test procedure is established to provide a uniform method for investigating the effect of operating temperature on the life expectancy of liquid-immersed transformers. The test procedures are intended to provide data for the selection of a limiting hottest-spot temperature for rating purposes, provide data which may serve as the basis for a guide for loading, and permit the comparative evaluation of a proposed insulation system with reference to a system that has proven to be acceptable in service.

8.1.3 TAPPI T 573pm-03 "Accelerated temperature ageing of printing and writing paper by dry oven exposure apparatus"

This test method describes a laboratory procedure for accelerating the ageing of printing and writing paper in sealed glass tubes through exposure to elevated temperature in an oven.

The test method applies to all types of printing and writing paper whether it is plain base paper, has internal additives, is coated, is printed or contains any variants of printing and writing paper found in normal usage. The method specifies the sample preparation and conditions of exposure required to obtain information on the stability of paper to ageing with regard to changes in mechanical strength properties brought about by exposure of such paper to elevated temperature. The method provides the means to compare the stability of different papers on a relative basis, but does not attempt to project the exact life expectancy for a given paper. Life expectancy depends in large part on the limits of acceptability beyond which various paper properties are no longer useful, as defined by end-users. For a given paper, those limits will be different for different end-users. This method does not provide a means to measure or to calculate such life expectancy.

8.2 LABORATORY SCALE EXPERIMENTS

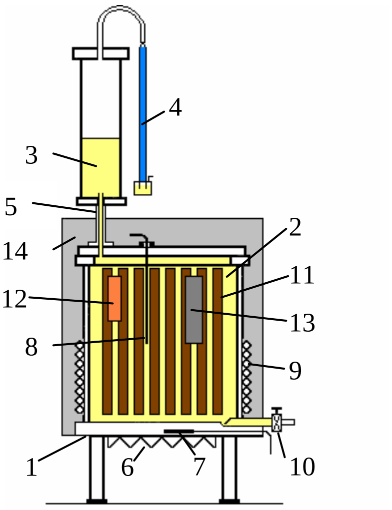
Laboratory experiments are typically conducted in sealed glass vials of only few hundred millilitres. The amount of aged paper is accordingly small. For the ageing, the vials are placed in an oven with forced air circulation. The following parameters can be varied in such experiments:

- Temperature
- Time
- Ratio cellulosic insulation - oil
- Air / oxygen / nitrogen blanket
- Water content of oil / cellulose
- Acid number of oil
- Addition of potential catalysts (copper / steel)
- Oil type (non inhibited / inhibited; new / preaged)
- Paper / board type (Thickness, density, upgraded)
- Addition of molecular sieve or other drying agents

8.3 SIMULATION OF REAL TRANSFORMERS E.G. WEIDMANN TEST APPARATUS

8.3.1 Principle

The concept underlying the design of the ageing vessels and the test procedure was to create conditions similar to those encountered in transformers. The mass and surfaces in the thermal model experiments are similar to those in a 200 MVA transformer [2]. The long term test vessels are constructed as shown in Figure 38. A vessel consists of 9 independent ageing chambers, which are heated or cooled jointly.



1: Ageing vessel with nine independent test chambers
2: Test chamber (volume: 20 dm^3; wall area: 60 dm^2 made of sand blasted steel sheet)
3: Expansion glass tube
4: Silicagel conservator
5: Flow baffle
6: Heater
7: Sensor for temperature control
8: Temperature measurement
9: Cooling coils
10: Outlet valve
11: Material samples (specimens)
12: Copper sheet; surface: 3 dm^2
13: Core steel; surface: 6 dm^2
14: Thermal insulation

Figure 38: Ageing vessel with open expansion system.

8.3.2 Expansion systems

Open expansion system: Some of the ageing vessels are operated using the concept of "open expansion". In this system, the oil in the expansion vessel is continuously in contact with dry air via a silica gel dryer and an oil filled bubbler.

Closed expansion system: In this case the expansion vessel contains a hermetic seal in the form of metal bellows, which completely isolates the oil/solid insulation from the atmosphere.

8.3.3 Temperature control

This system can be run with constant temperature as well as with temperature cycles. In case of temperature cycles the heating is switched off for e. g. 2 hours per day. During the cooling phase, the temperature in the chamber drops by 40 to 60 K depending on the nominal temperature.

8.4 SLOW THERMAL RAMPING

Isothermal testing of polymer ageing requires long-term exposure if realistic results are to be obtained, which means a timeconsuming and hence expensive exercise, which may have to be repeated many times over many different conditions. Rates of ageing can be accelerated by increasing the temperature of tests or by using a more aggressive environment, but then results must be extrapolated to working conditions, assuming that the same mechanisms still apply. Slow thermal ramp technique, similar to thermo-gravimetric analysis, allows the qualitative and, in some cases, quantitative assessment of ageing to be made in a relatively short time: 15 to 20 days, compared to up to 2 years for isothermal tests. The degree of polymerisation is used as a key indicator of degradation. [138,139].

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