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Improved Determination of Moisture in Oil-Paper-Insulations by Specialised Moisture Equilibrium Charts

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Abstract: This investigation discusses the influences of temperature, initial moisture content, type of cellulose and ageing state of cellulose and oil on moisture equilibrium in oil-paper-insulations. The equilibrium diagrams were derived by comparison of moisture relative to saturation in cellulose and oil. A special emphasis is given to the reliability of coulometric Karl Fischer titration to measure moisture in cellulose and oil. It was found, that especially the aging state (e.g. reflected by acidity) of insulating oil has a very strong impact on moisture receptivity and therefore on equilibrium state. The old method to derive moisture in cellulose (in %) from moisture in oil (in ppm) via an equilibrium diagram is effected by essential errors. Accuracy is considerable increased, if moisture in oil relative to saturation level (in %) is used instead of moisture in oil by weight (in ppm).

INTRODUCTION

Reliable assessment of the ageing state of high voltage power transformers is a basic condition for a failsafe and cost-saving service. Moisture in cellulose and oil is an ageing indicator and gains importance since utilities are ought to keep transformers in service even if the estimated life cycle is exceeded. Water receptivity of oil and cellulose changes with temperature. This relation is represented in moisture equilibrium diagrams. The load cycles of power transformers cause a continually exchange of water between paper/pressboard and oil. There is only a small number of investigations regarding moisture equilibrium and moreover they imply solely new materials. Hence this investigation involves aged materials too. The results enable for a more precise evaluation of moisture in paper and pressboard of HV-transformers.

WATER SOLUBILITY IN CELLULOSE AND OIL

Insulation oil Pure mineral transformer oil consists of saturated hydrocarbons such as paraffins and naphthenes. Because of their nonpolar molecule structure that is not able to coalesce a Van Der Vaals bond nor a hydrogen bond pure oil cannot dissolve any water. However insulation oil in power transformers is polluted by remains from refinery, ageing byproducts and cellulose particles. Thus water can be dissolved and exists in the following states:

- Bonded to ageing byproducts by Van Der Vaals and hydrogen bonds
- Absorbed by impurities e.g. cellulose fibers
- When the saturation value is exceeded, water will form a suspension with small drops.

The empiric Arrhenius equation describes the dependence of water saturation level $C_{W,S}$ on temperature T, there C_{Oil} and B are oil specific constants [1].

$$C_{W,S} = C_{Oil} \cdot e^{-\frac{B}{T}} \qquad (1)$$

The moisture content C_W is usually specified in ppm (µg water / g oil) or related to the saturation value in %.

$$C_{W,rel} = \frac{C_W}{C_{W,S}} \cdot 100\% \qquad (2)$$

Ageing of mineral oil Hydrocarbons in the oil are oxidized with a rate depending among others on oxygen level, temperature and moisture. Ageing products are alcohols, aldehydes, ketones and finally acids. All of these oxidation products are polar by nature and able to coalesce Van Der Waals and hydrogen bonds and thus to dissolve water. Van der Waals bonds base on interactions of dipoles (attraction of opponent charges). At a hydrogen bond one hydrogen atom (proton) is bonded between two atoms with a high electronegativity, see Fig. 1. This bond occurs between water and oil ageing products and between free water molecules too so that water forms drops if the saturation level is transgressed.

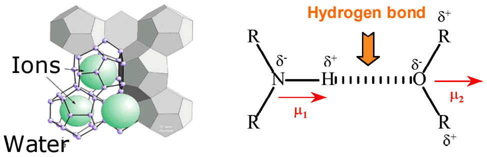

Fig. 1: Examples of Van Der Waals (left) and hydrogen bonds (right)

Because ageing products in mineral oil are able to dissolve water, the water solubility and saturation level will increase with ageing.

Cellulose Glucose rings forming long chains are used in oil-paper-insulations as pressboard, Transformerboard (made by Weidmann), Kraft paper (insulation paper) and thermally upgraded paper. Cellulose consists of polar glucose chains and is therefore able to dissolve high quantities of water in the following states:

- Bonded by Van Der Vaals and hydrogen bonds to glucose chains, water molecules may form multiple layers attracted to glucose chains
- As free water in capillaries

The ability to dissolve water is, depending on temperature, some thousand times higher compared to oil. The following example clarifies this relation: An transformer of 150 MVA, 400 kV has about 7 t cellulose and 80000 l oil. Cellulose stores at $C_W = 3$ % about 220 kg water and oil at 20 ppm only around 2 kg [2]. Insulation oil thus serves as a transport medium, not as a storage medium of water.

Ageing of cellulose The ageing processes of cellulose occurring in power transformers are depicted in the following table.

Reaction	Oxidation	Hydrolysis	Pyrolysis
Supposition	Oxygen	Water, acid	High temperature
Activation energy [KJ/mol] [3]		37-163 (at C_W=4-0,5 %)	230
Products	Water	Furans, water, decreased DP	Decreas. DP, furans, water, acids, CO_X

Hydrolysis is the dominating ageing process since pyrolysis takes place only at more excessive temperatures. Hydrolysis decreases the degree of polymerisation (DP, number of jointed glucose rings per cellulose chain, see Fig. 2) from 1000-1500 to 200-400 at the end of the cellulose life span.

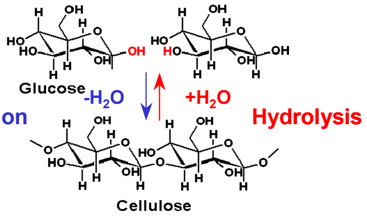

Fig. 2 Chaining through condensation and breakdown through hydrolysis of glucose rings

Sources of water in power transformers During the production process the cellulose parts of the main insulation (insulation paper, pressboard, supporting constructions) are dried under vacuum down to $C_W = 0{,}5$-1 %. Water arises from residual moisture in bulky construction elements, out of the atmosphere (breathing at open conservator systems, through leaky seals, during repair) and from hydrolysis [1]. The atmosphere is considered to be the main source of water.

MOISTURE DIFFUSION AND EQUILIBRIUM

Moisture diffusion is driven by a simple physical law: The *relative* moisture content $C_{W,rel}$ in adjacent materials becomes equal under equilibrium conditions.

$$C_{W,rel,Cel} = C_{W,rel,Oil} = C_{W,rel,Air} \tag{3}$$

With increasing temperature the ability of oil to dissolve water increases conspicuously, while that of cellulose decreases slightly. Thus a change in temperature causes a moisture diffusion process until equilibrium is reached.

Investigations in [1] and [2] led to an empiric equation to calculate the diffusion time constant τ. Because of some simplifications it gives only a rough estimation. Since the desorption of water molecules needs some energy to unfasten chemical bonds the desorption time constant is greater than the adsorption time constant.

$$\tau = \frac{d^2}{\pi^2 \cdot D} \tag{4}$$

d – thickness of pressboard
D – diffusion coefficient with

$$D = D_0 \cdot e^{0,5C + E\cdot(T_0^{-1} - T^{-1})} \tag{5}$$

$T_0 = 298$ K
$E_a = 8140$ K, $D_0 = 2.62\ 10^{-11}$ m²/s oil free
$E_a = 8074$ K, $D_0 = 1.34\ 10^{-13}$ m²/s oil immersed

For $C_{W,Pb} = 0{,}5$ % and $d = 1$ mm the coefficients give the time constants in the following table [2]. The results show, that for oil impregnated pressboard (in power transformers) at low temperatures the equilibrium is hardly ever reached.

Pressboard	oil free		oil impregnated	
Temperature	20°C	70°C	20°C	70°C
Time constant τ	1,7 h	0,03 h	333 h	6 h

MEASUREMENT TECHNIQUE

Coulometric titration by Karl Fischer

Titration basically means to add a reagent of known concentration (titre) to a unknown substance until the concentration is balanced. At *volumetric* titration the added volume is measured and the demanded value (here water content) is calculated by a stoichiometric equation. The sensitivity of volumetric titration is limited to some 10 µg water so that it is not applicable for dry insulation oils used in power transformers. At *coulometric* titration the titre is added by a generator electrode. Water content calculates equation (6). The detection limit of coulometric titration reaches down to some µg of water.

$$2\ H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2\ HI \tag{6}$$

The moisture of the material could be brought into the reaction vessel by three methods:

Firstly it is possible to inject the material directly into the reaction vessel, e.g. oil through a syringe. This method pollutes the reagent and side reactions of ageing products or inhibitors with the reagent are possible. E.g. it is known, that aldehydes and ketones react with the methanol of the reagent to acetales and ketales with water as a byproduct.

Secondly the water can be dissolved in another medium, e.g. methanol. This is applicable for cellulose samples. The sample will be immersed into methanol, that will extract the water out of the cellulose. The methanol and water will then be injected into the reaction vessel.

Thirdly the sample can be heated in an external oven and a gas stream with water vapour is lead into the reaction vessel. Advantageously the reaction vessel remains clean from pollutions and also from ageing byproducts, depending on their boiling point. A drawback of this method is the blank value of the gas stream and the heating vessel. This decreases the sensitivity compared to the direct injection method. The parameter heating temperature of cellulose samples led to some discussions in previous investigations. According to IEC 60814 it should be 130-140°C. The authors of [5] found out, that at pressboard samples only a temperature of higher than 180°C leads to results comparable to the methanol extraction method, see Fig. 3.

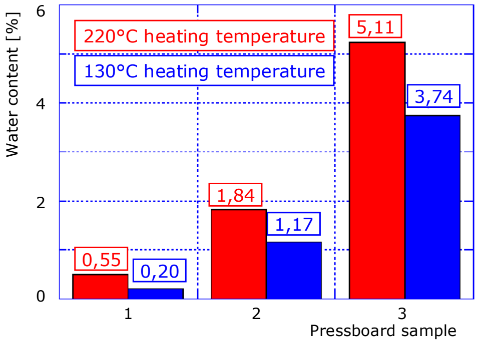

Fig. 3 Moisture content analysed by KFT with heating temperatures of 220°C and 130°C, [5]

Accuracy of Karl Fischer Titration Although KFT is counted as a reliable measurement method, it is effected by some influences: (1) There is always a moisture ingress from atmosphere during sample preparation. Therefore all results have a deviation to a higher moisture content. (2) For the heating method the blank value forbids moisture measurements in dry oils (below 20 ppm). Furthermore direct injection and heating method lead to different results for moisture in oil. This might be due to (3) the unknown influence of oil additives and ageing by products like described above. (4) Cellulose bonds water with chemical bonds of different strengths. Therefore a sufficient thermal energy to release the bonds is needed. It is however unsure, if all the water is released. (5) Heating temperature and time strictly changes the released water as depicted in Fig. 3.

In this investigation a coulometric Karl Fischer Titration instrument with heating oven and methanol vapour circulation in a closed loop called Aqua 40.00 made by Elektrochemie Halle was used. Water in cellulose is measured by the heating method with temperatures of 160°C for paper and 180°C for pressboard. For oil immersed cellulose it is necessary to discern between the weight of oil and of cellulose. Therefore the insulation oil was extracted from the cellulose by methanol after titration but before weighting. For water in oil determination the oil was directly injected into the reaction vessel by a syringe.

Using the described procedures the repeatability of moisture determination in cellulose was then ± 10 % of the measurement value in the range 0,3-8 % moisture by weight. For moisture in oil the repeatability is about ± 7 % in the range of 15-90 ppm moisture by weight.

Relative water content by capacitive probes

Capacitive probes consist of two electrodes with a dielectric made by a hydroscopic polymer, see Fig. 4. Water molecules penetrate into the polymer depending on the water content *relative to saturation level* of the ambient material. Water penetration *c* then changes of the capacity *C* because of the high relative permittivity of water $\varepsilon_r = 80$, see (7).

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot A}{d} \quad \text{and} \quad \varepsilon_r = \varepsilon_i + \varepsilon_w \cdot c \qquad (7)$$

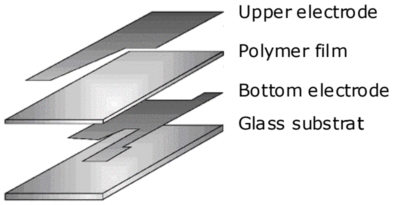

Fig. 4 Schematic drawing of a polymer thin film sensor

In this investigation two HMP 228 by Vaisala were used. The average value of both sensors was used for moisture determination. Moisture content relative to saturation level is the intrinsic measurement parameter of this sensor. However the moisture by weight in ppm could be delivered too by an arithmetic equation containing two constants A and B. These constants depend on water saturation level of the oil (e.g. ageing state, pollutions, kind of oil). Therefore to obtain reliable ppm-values the sensor must be calibrated for each oil-paper-system. Because of the different measurement techniques and values there is no direct comparability given to Karl Fischer Titration. In this setup only the original measurement value, the moisture content relative to saturation level, that is independent on oil ageing etc. was used.

MOISTURE EQUILIBRIUM DIAGRAMS

Investigated materials

Cellulose types explored were pressboard, Kraft insulation paper and thermally upgraded paper. To simulate ageing some cellulose samples were thermally degraded by heating at 130°C under wet air for 1 week. As oil types were used new Nynas Nitro 3000, new Shell Diala D and an oil aged by 25 years of service with an neutralization number of 0,08 mg KOH/g oil.

Establishing equilibrium diagrams

To measure moisture in cellulose and oil and establish equilibrium diagrams one may use a direct or an indirect method.

Direct method Oil and cellulose are in direct contact to each other, the cellulose is oil immersed. Measurements take part under different temperatures after equilibrium is reached by sampling of oil and cellulose. The Karl Fischer Titration method determines moisture content.

The fundamental drawback of this method causes the long time constants to establish equilibrium especially at lower temperatures. Beside this the Karl Fischer Measurements of moisture in oil are afflicted by measurement errors as described earlier. This leads to doubtful results of the direct method.

Indirect method This method bases on the physical law, that the relative moisture content for adjacent materials is equal under equilibrium conditions, see above. The ambient medium could be air or oil, supposed they are at the same temperature and pressure.

Thereto in a first step the relative moisture of air $C_{W,rel,Air}$ in equilibrium with cellulose is measured at different temperatures. The second step comprises in the measurement of the relative moisture in oil $C_{W,rel,Oil}$ at different temperatures. The third step is the combination of both diagrams under the fulfilled requirement, that the relative moisture in air is equal to the relative moisture in oil $C_{W,rel,Air} = C_{W,rel,Oil}$ under equilibrium conditions. This method was originally invented by T.V. Oommen [4].

Advantages of this method are, that equilibrium in oil free cellulose is established a 100 times faster compared to oil immersed cellulose, the moisture profile becomes more homogenous, it is much easier to measure moisture relative to saturation level (in %) than to measure moisture by weight (i.e. in ppm) and relative moisture can be determined continuously.

Equilibrium under new conditions

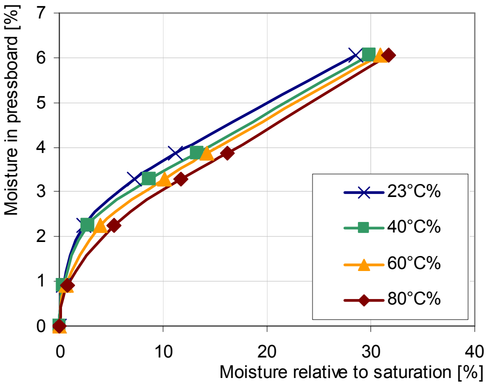

Fig. 5 Moisture in pressboard at different temperatures

Fig. 5 shows the moisture in new pressboard C_W as a function of moisture in pressboard relative to saturation value with temperature as parameter. It is obvious, that the relation relative moisture to moisture by weight is not linear but steep for low moisture contents and then rather flat for an increasing moisture content. This behavior could be explained by the way water is attracted to cellulose. Because of Van Der Waals bonds water molecules can form multiple layers. Beside this multiples layers of water at outer areas of cellulose may inhibit water molecules to diffuse deeper inside. Thus moisture distribution will be nonlinear.

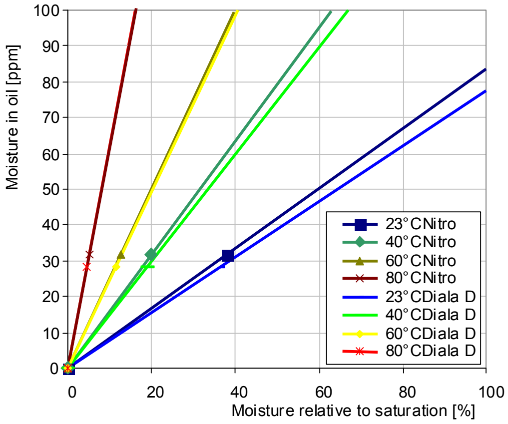

Fig. 6 Moisture in oil at different temperatures

Fig. 6 shows moisture in new Nynas Nitro 3000 and Shell Diala D. Both oils have only slight differences especially in the low temperature region. In contrast to cellulose the curves are straight lines because moisture absorption in fluids proceeds homogenously.

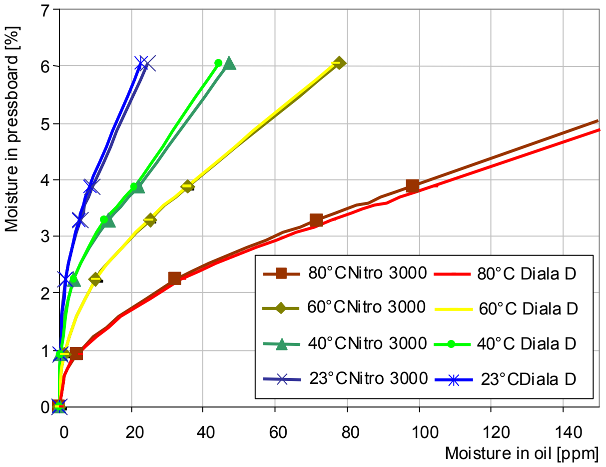

Fig. 7 Equilibrium diagram for new pressboard combined with new insulation oils

Another difference to the absorption in cellulose is, that for oils at increasing temperature the ability do dissolve moisture *increases* there that of cellulose *decreases.* This oppositional behaviour causes at power transformers, that for increasing temperatures moisture diffuses into the oil and for decreasing temperatures the other way round. Still the major part of moisture remains in the solid parts of the insulation such as pressboard, wood and paper.

To establish an equilibrium diagram, the moisture relative to saturation in Fig. 5 and Fig. 6 (x-axis) will be set as equal like described above. This leads to the equilibrium diagram for new pressboard and new insulation oil (Nynas Nitro 3000 and Shell Diala D) as depicted in Fig. 7. As already mentioned, the type of the new insulation oil has only a slight influence on equilibrium conditions.

Fig. 8 shows the moisture in new insulation paper (Kraft paper) and of thermally upgraded insulation paper as a function of relative moisture in paper. The ability of thermally upgraded paper to absorb moisture seams to be higher compared to Kraft paper and also to pressboard (Fig. 5), especially for the low moisture region. This is also represented in the equilibrium diagram Fig. 9 for new Kraft paper, thermally upgraded paper and new Nynas Nitro 3000.

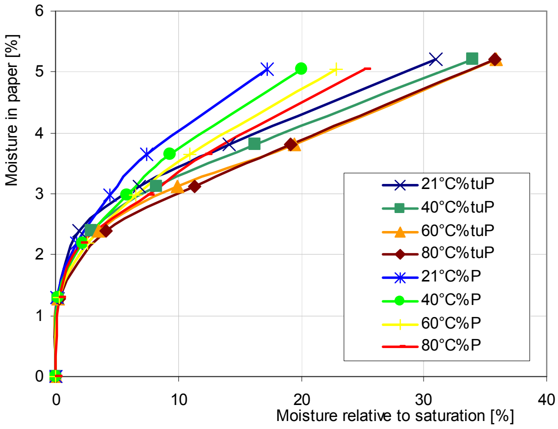

Fig. 8 Moisture in Kraft paper (P) and thermally upgraded paper (tuP) at different temperatures

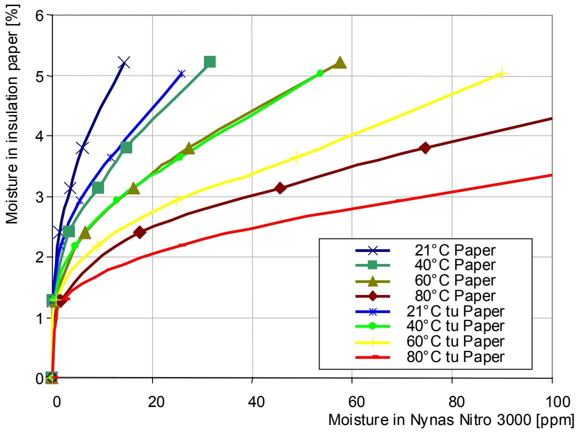

Fig. 9 Equilibrium for new Kraft paper (Paper) and thermally upgraded paper (tu Paper) combined with new Nynas Nitro 3000

Influence of ageing

Fig. 10 shows the moisture saturation level measured for new Shell Diala D and Nynas Nitro 3000 compared to that of an oil aged by 25 years of service. This aged oil can dissolve the double amount of water compared to both new oils.

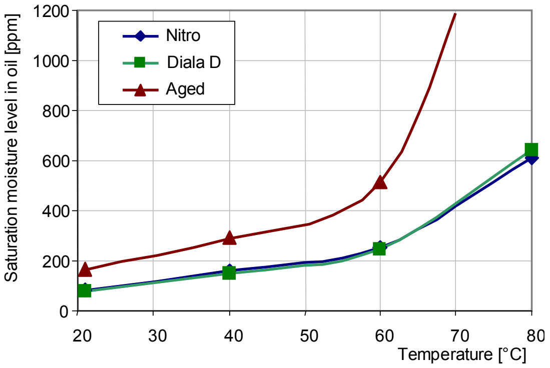

Fig. 10 Moisture saturation level for new Nynas Nitro 3000, Shell Diala D and a 25 years aged oil

As described above ageing byproducts change water solubility of oil and cellulose. Thereby this displacement means for oil an intense *increase* of water solubility and for cellulose a slight *decrease*. Therefore equilibrium conditions change too. The array of equilibrium curves for aged oil-cellulose-systems in Fig. 11 is shifted towards oil because of its increased water solubility.

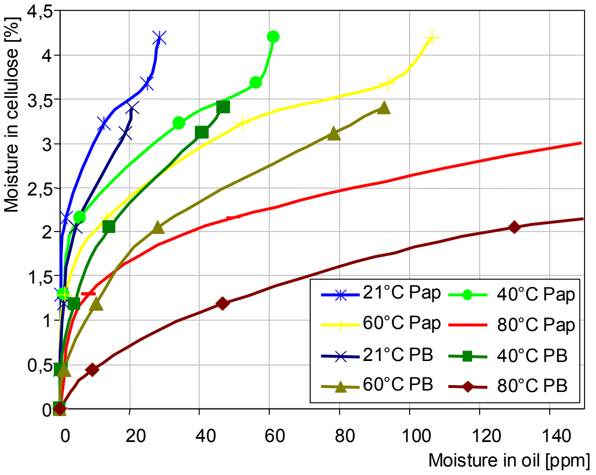

Fig. 11 Moisture equilibrium for thermally degraded paper (Pap) and pressboard (PB) with an aged oil

ESTIMATING MOISTURE IN CELLULOSE BY USE OF EQUILIBRIUM DIAGRAMS

Previous method

For many operators it is common to determine moisture in cellulose as an ageing indicator by the following method:

1. Sampling of insulation oil under service conditions

2. Determination of water content using Karl Fischer Titration
3. Deriving moisture in paper via equilibrium diagram

This procedure is effected by substantial errors:

1. Sampling, transportation to laboratory and moisture measurement via Karl Fischer Titration
2. Diagrams only valid under equilibrium conditions, (depending on temperature established after days/months)
3. Steep gradient in low moisture region (dry insulations)
4. Different results using different equilibrium charts (Oommen, Piper, Fabre Pichon)
5. Temperature and therefore moisture distribution in transformer winding with gradient of up to 30 K
6. Equilibrium depends on saturation level (established with new cellulose/oil, ageing changes saturation level)

All these errors lead to wide scattered results in determination of moisture in cellulose via moisture in oil. Mostly the results are higher compared to other measurement techniques.

Advanced method

An approach to improve equilibrium diagrams to evaluate moisture in cellulose is to use the moisture in oil *relative to saturation level* in % (see Fig. 5 and Fig. 8) instead of moisture by weight in ppm. Relative moisture in oil advantageously contains the influence of ageing and is easy and much more accurate measurable compared to moisture by weight in ppm. Some transformers are already equipped with moisture sensors for online monitoring purposes to measure relative moisture and temperature. The progression of temperature could be used to estimate whether equilibrium exists or not. Using the relative moisture in oil the errors 1, 2, 3, 6 of the list above can be neglected or at least reduced.

SUMMARY AND CONCLUSIONS

Main motivation for this investigation was to improve the knowledge about moisture equilibrium in oil-paper-insulations and to extend equilibrium diagrams also to aged conditions.

(1) Water in the oil-paper-insulation of power transformers is stored in cellulose, while oil serves as a transport medium.

(2) The ability to dissolve water changes especially with ageing of oil. Ageing products such as alcohols, aldehydes, ketones and acids are able to coalesce with water and therefore increase water solubility.

(3) Moisture diffusion and equilibrium depends on the physical law, that the *relative* moisture content $C_{W,rel}$ in adjacent materials becomes equal under equilibrium conditions.

(4) Moisture measurements by coulometric titration according to Karl Fischer are effected by ingress from atmosphere, procedure of sample injection, heating temperature and other influences.

(5) Equilibrium diagrams can be established by direct measurements or by comparison of relative moisture. The second approach is used in this investigation because of several advantages.

(6) Moisture equilibrium depends on kind of cellulose (paper, pressboard) but only slightly on type of oil.

(7) Ageing shifts the array of equilibrium curves towards oil because of its intense increased water solubility thereby that of cellulose decreases slightly.

(8) The old method to derive moisture in cellulose (in %) from moisture in oil (in ppm) via equilibrium diagram is effected by essential errors. Better results can be obtained, if moisture in oil relative to saturation level (in %) is used instead of moisture in oil by weight (in ppm).

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