Aging of Oil-Impregnated Paper in Power Transformers

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***Abstract*—The effects of moisture, oxygen, and acidity upon the aging of Kraft and thermally upgraded ("Insuldur®") papers have been studied in detail. The results for Kraft are consistent with the kinetic model and parameters proposed earlier by Emsley *et al.*, and with the principle that moisture promotes acid-hydrolysis by causing carboxylic acids to dissociate. Moisture is released during the aging of Kraft and, hence, its aging is auto-acceleratory. In contrast, Insuldur consumed moisture under the same conditions, aged more slowly, and its aging was less accelerated by added moisture. 2-Furfuraldehyde (2FAL), which is a dehydration product of pentosans and, hence, an index of moisture production, is also released from Kraft during aging, but not from Insuldur. Acids are, however, produced from both types of paper. Theoretical explanations for these findings are proposed, and their practical implications for transformer maintenance are discussed.**

***Index Terms*—Acids, aging, hydrolysis, maintenance, oil, oxidation, paper, transformer, 2-Furfuraldehyde, water.**

I. INTRODUCTION

THE population of power transformers is growing older. Once regarded as "slumbering giants," requiring no particular attention, they are becoming a source of concern to utilities as the incidence of outages and explosions increases. This concern is exacerbated by the transformers' high current value, their long outage times, the high cost of replacing them, and the serious consequences of system failure. To minimize the need for reinvestments and costly maintenance, and to plan rationally for the future, it is essential to understand and quantify the aging kinetics and to learn how they may be controlled.

In this context, the windings are the most vulnerable part of the transformer. The winding insulation system is subject to irreversible and significant aging. Although failure rates are still low, one can foresee a future in which aging of the cellulosic insulation system has resulted in a reduced ability to withstand the mechanical stresses occurring during inrush currents and external short circuiting. The problem is accentuated by changes in operational conditions, including increases in acidity and humidity, increased loading, and short-circuit power.

Several significant experimental studies have established that temperature, moisture, and oxygen are major factors influencing the aging of cellulose in transformers [1]–[6].

This paper describes aging experiments on oil-impregnated paper, carried out under conditions directly relevant to the practical situation. Also included are some experiments simulating oil reclaiming during the aging process. The materials studied are those most frequently used in transformers in Norway: Kraft paper and thermally upgraded (Insuldur®) paper, impregnated with inhibited naphthenic oil. These experiments, together with a discussion on transformer maintenance, are also described in an internal report [7].

II. CELLULOSE CHEMISTRY

Kraft paper consists of cellulose, hemicellulose, and some residual thiolignin that has escaped complete removal during the Kraft pulping process. The cellulose consists of linear, polymeric chains of cyclic, β-D-glucopyranosyl units. The number of such units per chain is called the degree of polymerization (DP). Cellulosic chains associate in both crystalline and amorphous regions to form microfibrils, which again form fibrils and finally fibers. Most of the mechanical strength of the paper is due to its content of these fibrils and fibers, while the hemicellulose and residual lignin are amorphous, gummy substances that serve to cement them together [8]. The aging process is essentially one of depolymerization, brought about by acid-hydrolysis, pyrolysis, and oxidation. It is commonly acknowledged that a high acidity in the oil will accelerate aging. When the inter-unit linkages in cellulosic chains are cleaved, the DP-value is reduced and the mechanical strength of the cellulose decreases. Often the number of chain scissions (η); $\eta = DP_{\text{new}}/DP_{\text{old}} - 1$, is used to describe aging. Here DP_{old} and DP_{new} are, respectively, the DP-values after and before an aging period. The amorphous regions of the cellulosic fibrils are more readily cleaved than the crystalline ones, and the hemicellulose is also especially susceptible to chemical attack. When new, the paper will have a DP of about 1200. After going through the factory drying process, the paper in a transformer will have a DP of about 1000 and a water content around 0.5%. It is commonly accepted that when the DP has fallen to about 200, the tensile strength of the paper has dropped to 20% of its original value, and the inter-fiber forces have also diminished [9]. To retard aging, one can thermally upgrade the paper by linking bulky substituents such as cyanoethyl ether groups to the HO-groups in the cellulose and hemicellulose; or add weak, organic bases such as dicyandiamide, urea, or melamine (a cyclic trimer of urea) so as to neutralize acids produced by oxidation of the oil and paper. It should be noted that these bases are themselves subject to acid-hydrolysis (the end-products in each case being carbon dioxide and ammonia), and water is consumed at every step; hence, they may be considered as organochemical drying agents as well as bases.

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An extensive literature survey was conducted in 1994 [10]. He concluded that a so-called "thermally activated" kinetic process can describe paper aging

$$\frac{1}{DP_{\text{old}}} - \frac{1}{DP_{\text{new}}} = A \cdot e^{(-E/R(T+273))} \cdot t. \qquad (1)$$

where T is the temperature, E the activation energy, A a parameter depending upon the chemical environment, R the molar gas constant, and t the elapsed aging time. The model assumes that the aging kinetics is due to one single mechanism, in which the activation energy describes how the aging rate depends upon temperature. Emsley found values for E and A, and suggested that they may be used for estimating the lifetimes of transformers.

To interpret the aging data correctly, it is essential to understand the mechanism of acid-hydrolysis. By using methyl β-D-glucopyranoside and cellobiose as model substances, it has been shown that the hydrolysis is specific-acid catalyzed and unimolecular [11], [12]. This means that it is catalyzed exclusively by hydrogen ions from dissociated acids; undissociated carboxylic acids do not depolymerize cellulose. It is the H+ concentration that matters, not the total acid concentration (or neutralization value). It also means that water does not participate in the rate-controlling step. Water does, however, affect the H+ – concentration by causing carboxylic acids to dissociate, and in this way it exerts a profound influence upon the aging process.

When the inter-unit linkages in cellulose or xylan (the principal hemicellulose in hardwood pulps and a major one in softwood pulps) are hydrolyzed by acid, one molecule of water is *consumed* for every linkage cleaved. When, however, the activity of water in the system is very low, and especially when the temperature exceeds 100 °C as in the present case, acid-hydrolysis of internal linkages is followed, relatively rapidly, by a series of acid-catalyzed dehydration reactions leading to the *release* of three molecules of water from every monosaccharidic unit. There is therefore a net production of two molecules of water per unit. The carbon skeleton of the sugar unit is simultaneously converted into a derivative of furan. Xylan yields 2-furfuraldehyde (furfural), which is fairly stable to acid, so that its measurement can be used to provide an arbitrary index of water release. Cellulose yields 5-hydroxymethyl-2-furaldehyde (hydroxymethylfurfural). This is not so stable, and it decomposes further into lævulinic acid and formic acid [13]. It should be noted that these acids are produced nonoxidatively from neutral sugars; they will therefore increase the acidity of the system, and accelerate that part of the aging process that is attributable to acid-catalyzed hydrolysis and dehydration reactions. At higher temperatures, however, formic acid will dissociate into carbon monoxide and water. Lævulinic acid polymerizes readily to yield a dark-brown, acidic polymer often referred to as "caramel." This material, together with the residues of thiolignin mentioned earlier, probably makes up a part of the sludge that accumulates in aged transformer oils.

The second major cause of paper aging is oxygen. It is essentially a form of pyrolysis or "slow combustion," since its end-products are water and carbon dioxide. There are, however, many intermediates in the oxidative process. Three of them, 2-furfuraldehyde, 5-hydroxymethyl-2-furaldehyde, and carbon monoxide [14], are also produced nonoxidatively as described above [13]. Others seem to be produced exclusively by oxidation, and their identities therefore have diagnostic significance. They include 5-methyl-2-furaldehyde, 2-acetylfuran, 2-hydroxymethylfuran (furfuryl alcohol) as previously reported [15]. Oxidative depolymerization is catalyzed by hydroxy-radicals (HO•), which are produced by decomposition of hydrogen peroxide H_2O_2. 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 in a reaction catalyzed by traces of Fe^{3+} together with small amounts of autooxidizable compounds such as phenols or aromatic amines or thiols. These are especially significant because aromatic thiol groups are introduced into the lignin during the Kraft process. Phenolic groups are also formed by oxidation of aromatic compounds in the oil, and are also present through the addition of antioxidants (di-t-butylparacresol), though there is no evidence at present that the latter has any detrimental effect. (It should be emphasized that the level of *iron* and the *acidity* in the system determine whether or not a phenol generates more hydroxy-radicals than it captures.) The production of hydroxy-radicals is suppressed by acids and promoted by alkalis.

III. EXPERIMENTAL DESIGN AND PROCEDURES

The aging experiments were performed on paper strips (121 × 12 mm) cut from: a) Kraft paper (Munksjø) of 19 layers per millimeter and weighing 75.8 mg per strip; or b) thermally upgraded, microcreped paper from Avery Dennison ("Insuldur"), of 14 layers per millimeter thickness, and weighing 122.4 mg per strip.

The strips were dried *in vacuo*, first at 23 °C (two days) and then at 100 °C (two days). Portions (100 g, comprising 1300 strips of Kraft, or 820 of Insuldur) were enclosed with transformer oil (1.8 kg) in glass bottles (2.32 L) fitted with lead-sealed screw caps. In cases where water was added, it was first equilibrated with the paper before the oil was added. The oil was normally a dried and degassed naphthenic, inhibited oil (NYTRO 10X), but in one series, an acidic oil (neutralization equivalent, 0.16 mg KOH/g) from a service-aged transformer was used. The bottles were kept in cabinets, thermostatically maintained at 70°, 90°, 110°, or 130 °C, and both paper and oil were sampled throughout the aging period. Each time an oil sample was taken, an equal volume (60 ml) of dried and degassed oil was injected into the test bottle, and the free space was flushed with argon to remove oxygen (except when oxygen was added).

A. Aging Experiments

Aging experiments were carried out under six different test conditions for both types of paper to investigate how the aging rates depend upon transformer conditions:

- dry paper with filtered and degassed oil (A);
- dry paper with filtered and degassed oil, plus 150-g molecular sieve (3A) to absorb water (B);
- dry paper with used transformer oil having an acidity of 0.16 mg KOH/g (C). This acidity was reduced to 0.14 mg KOH/g by the paper;

TABLE I
INITIAL AMOUNT OF WATER (% WEIGHT) IN PAPER FOR EXPERIMENTS ON KRAFT AND UPGRADED PAPER

Experimental condition	Water added to paper [%]	In Kraft paper [%]		In upgraded paper [%]	
		From oil sample	Meas. in paper (20°C)	From oil sample	Meas. in paper (20°C)
Dried paper	0	0,2	0,05	0,2	0
Molecular sieve	0	-	0,05	-	0
Acidic oil	0	0,2	0,4	0,2	0,1
Oxygenated oil	0	0,2	0,03	0,2	0,1
Medium water cont.	1,0	1,5	1,5	1,0	0,7
High water cont.	3,1	4,0	4,1	3,5	3

From oil sample: Calculated via equilibrium curves from content in oil.

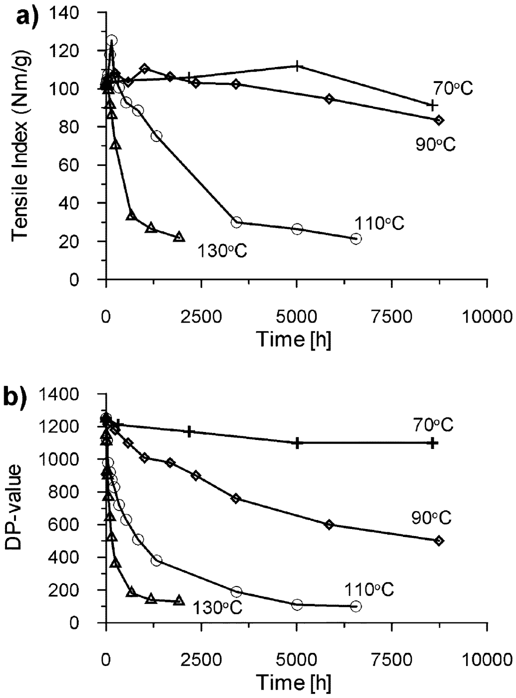

Fig. 1. Tensile index (a) and DP value (b) for Kraft paper versus time; 3% moisture added.

- dry paper with filtered and degassed oil, with repeated exposure to dry air at a pressure of 2 bar for half an hour about every 14 days to get a high oxygen content (D);
- paper with 1% water added (by weight) and filtered and degassed oil (E);
- paper with 3% water added (by weight) and filtered and degassed oil (F).

For the series with water added to the paper, this was done simultaneously with both types of paper. An overview of moisture conditions is given in Table I.

Moisture in oil was measured on 2.5-ml samples by Karl Fischer titration, using a Metrohm 737 KF Coulometer with a 703 TI stand.

Acidity in oil was measured on samples (20 g) according to IEC 60296, by titration with KOH and an Alkali Blue indicator.

2-Furfuraldehyde (2FAL) in oil was measured on samples (10 ml) by Electroinstitute Milan Vidmar in Slovenia.

Moisture in paper was measured on one paper strip taken from the hot test bottles. The samples were transferred as quickly as possible to the moisture extraction oven (Metrohm 768 KF) and moisture was thereafter measured with the Karl Fischer equipment. At 3% moisture in paper, the samples showed a moisture loss of 9% and 20% when taken from test bottles at 70 and 130 °C, respectively, [16] due to evaporation during transfer.

Acidity of paper: Four paper strips were kept in 20 ml of distilled water for three days at room temperature to extract the acidic compounds from the paper. A portion (10 ml) of the extract was then titrated as for the oil samples.

The tensile strength of the paper was measured using a mechanical test machine with a jaw separation of 100 mm. The machine measures the force required to stretch a paper strip to breakage and the percentage elongation. The following parameters were recorded: tensile index, percentage elongation at break, tensile energy absorption index, and the modulus of elasticity index (similar to Young's modulus/density). Each test was done on ten strips.

DP values were measured on six paper strips according to IEC 60450.

B. Attempted Transformer Renovation

In a separate experiment, Kraft paper samples were prepared and distributed in eight bottles in the same way as described above. Water was added to a humidity of 2.5% in the paper. The bottles were placed in a heating cabinet at 110 °C, and aging was continued until the paper was expected to have DP ~600. The bottles were cooled and divided as follows:

- two bottles were not treated (reference samples);
- the oil in two bottles was replaced with clean and dry oil;
- oil was removed and the paper dried *in vacuo* (three days at 23 °C, then two days at 80 °C) for two bottles prior to refilling with clean and dry oil;
- oil was removed from two bottles and the paper put into distilled water for several days to remove acidic compounds. Then, the paper was dried under vacuum at a temperature of 80 °C and reimpregnated with clean and dry oil.

Further aging and measurements were then continued as before.

IV. RESULTS

A. Aging Experiments

Figs. 1 and 2 show the effect of temperature on aging when the paper contains sufficient moisture to promote dissociation of the carboxylic acid groups in the oil and paper; and also the greater susceptibility of Kraft compared to Insuldur.

Measurements of tensile strength show more scatter for the microcreped Insuldur than for Kraft, but their relationship to DP is clear for both papers (Fig. 3).

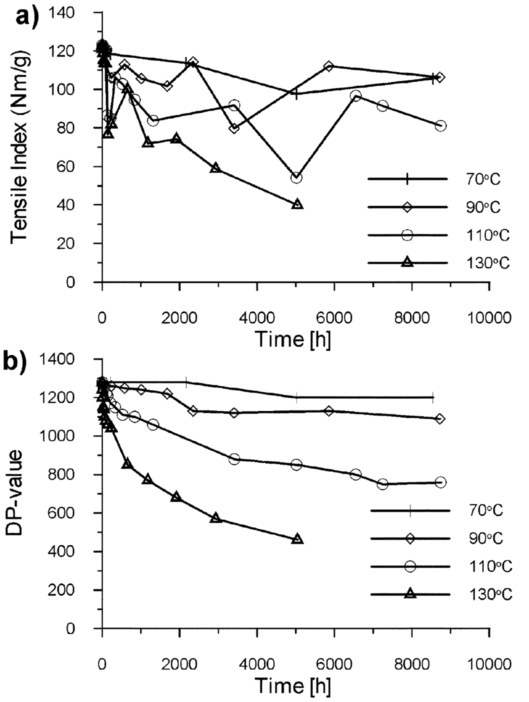

Fig. 2. Tensile index (a) and DP value (b) for Insuldur paper versus time; 3% moisture added.

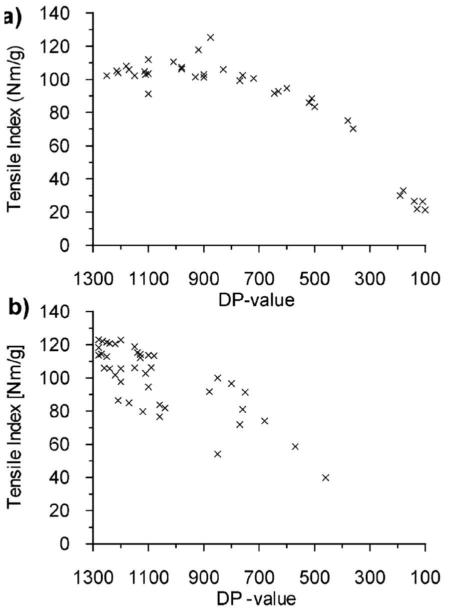

Fig. 3. Correlation between tensile index and DP value for (a) Kraft and (b) Insuldur.

As shown by Emsley *et al.*, [9] plotting the inverse of DP versus aging time gives straight lines whose slopes show the speed of aging; the aging rate k being the slope of the line. Within the range of interest, $1/DP < 0{,}005$ (i.e., $DP > 200$), we found the relation to be linear as shown in Fig. 4.

Whereas the initial aging rate is representative for the interesting range, the rate decreased at DP values <200. This may be because the amorphous regions of the cellulosic fibrils are cleaved first due to their greater permeability, while the crystalline regions are attacked more slowly.

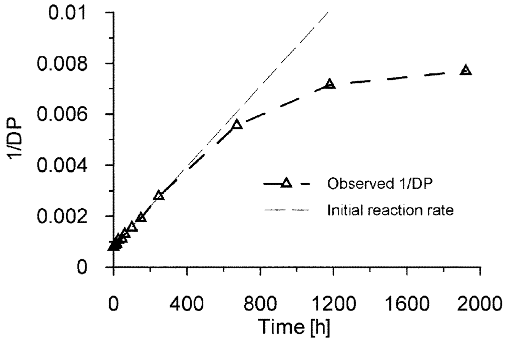

Fig. 4. Aging as a function of time.

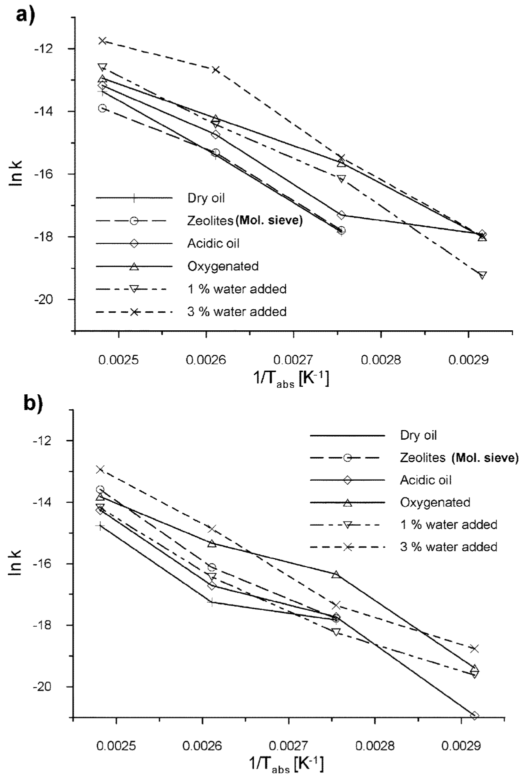

Fig. 5. Arrhenius plots for Kraft (a) and Insuldur (b), based upon initial aging rates (k). The data points represent (from the left) temperatures of 130, 110, 90, and 70°C.

Measurement of the initial aging rate (k) over a range of temperatures [Figs. 1(a) and 2(a)] made it possible to construct Arrhenius plots by plotting the natural logarithms of the aging rates versus the inverse of the absolute temperature (Fig. 5). The data for 70 °C are uncertain, as aging was very slow at this temperature. The plots are otherwise reasonably straight, suggesting that the aging mechanism was independent of temperature within the range of interest. The temperature dependence can be used to calculate the activation energy from equation (1).

When the activation energy is calculated from all of these curves—excluding the uncertain data points for 70 °C and disregarding probable differences in activation energy between oxidation and hydrolysis—values for Kraft and upgraded paper, respectively, of 114 and 110 kJ/mol are obtained.

By assuming an activation energy of 111 kJ/mole in all cases (as proposed by Emsley *et al.* [10] and confirmed in this inves-

TABLE II
PRE-EXPONENTIAL (A) FACTOR ESTIMATED FOR AN ACTIVATION ENERGY OF 111 KJ/MOL

Test Conditions	Emsley's Data		Present investigation	
	Kraft Paper E = 111 kJ/mole	95 % conf. bounds	Kraft Paper E = 111 kJ/mole	Insuldur E = 111 kJ/mole
Dry & clean	$1{,}07\times10^{8}$	$0{,}2\text{-}4{,}7\times10^{8}$	$2{,}0 \pm 0{,}5\times10^{8}$	$6{,}7\pm1{,}4 \times10^{7}$
Mol. Sieve			$2{,}1\pm 0{,}2\times10^{8}$	$3{,}1\pm2{,}1 \times10^{8}$
Acidic oil			$2{,}4\pm 0{,}7\times10^{8}$	$1{,}1\pm0{,}6 \times10^{8}$
Oxygen	(2×10^{8})		$8{,}3\pm 2{,}8\times10^{8}$	$3{,}5\pm 1{,}4\times10^{8}$
1% water	$3{,}5\times10^{8}$	$0{,}8\text{–}15\times10^{8}$	$6{,}2\pm 2{,}9\times10^{8}$	$1{,}1\pm0{,}5 \times10^{8}$
2% water	$7{,}8\times10^{8}$	$1{,}8\text{–}33\times10^{8}$		
3-4% water	35×10^{8}	$0{,}8\text{–}16\times10^{9}$	$21{,}0\pm 7{,}8\times10^{8}$	$2{,}6\pm 1{,}7\times10^{8}$

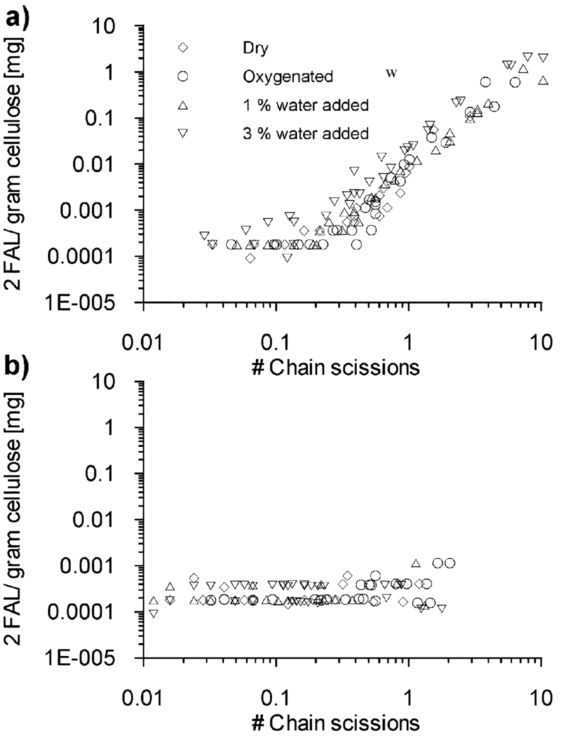

Fig. 6. Concentration of 2FAL for (a) Kraft and (b) Insuldur.

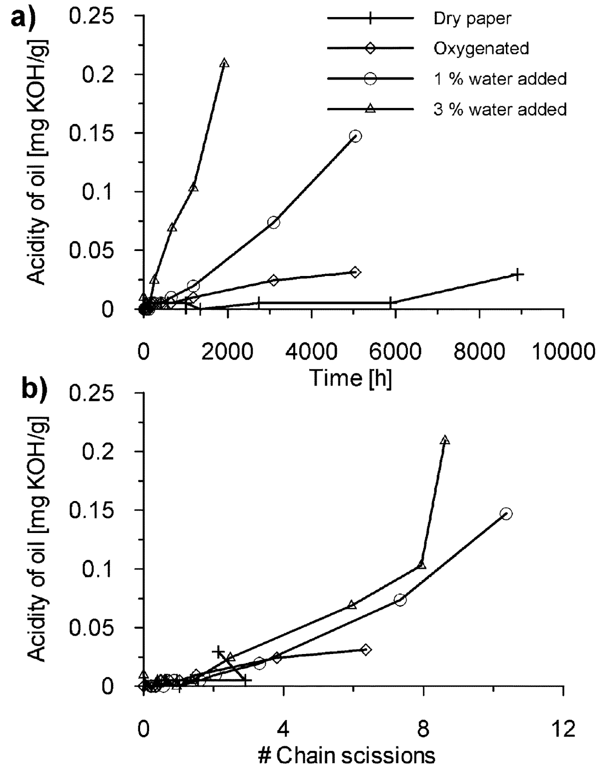

Fig. 7. Acidity of oil in experiments on Kraft paper at 130 °C: (a) development with time, and (b) correlation with chain scissions.

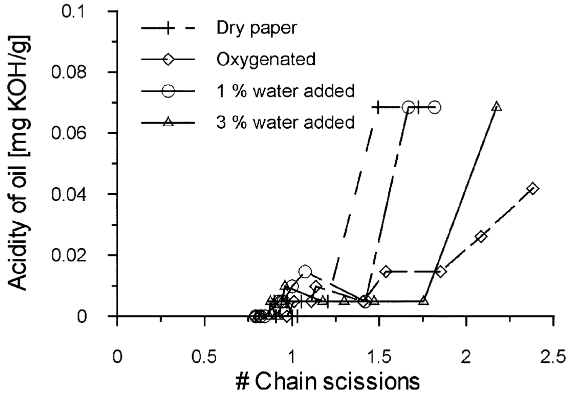

Fig. 8. Acidity of oil in experiments on Insuldur at 130 °C: correlation with chain scissions.

tigation), the corresponding A-values can be estimated from a linear regression. The results are shown in Table II.

B. Chemical Byproducts From Aging

During the experiments, the production of 2FAL, acidity, and moisture were all measured. Fig. 6 shows the production of 2FAL per gram of cellulose for the series with dry and clean oil, and for those with oxygen and water added.

The 2FAL concentration increases for Kraft and remains low and stable for Insuldur. For Kraft, the 2FAL production increases with humidity. The service-aged oil initially contained 0.64 mg/kg of 2FAL, but when it was used together with Insuldur, the 2FAL concentration decreased with time.

Fig. 7 shows how the acidity in the oil increased with time for Kraft at 130 °C. Plots of acidity versus chain scissions show that the acid production is virtually linear with aging. Upon comparing the total (combined) acidity in paper and oil for Kraft and Insuldur, it is found, however, that acid production is greater with the latter (Fig. 8).

Because of problems with evaporation as detailed in the experimental section, direct measurements of moisture in paper gave inconsistent results and were therefore discarded. The measurements of water in oil were, however, found to be reliable. The amount of water in the paper was therefore estimated from equilibrium curves for water in a combined paper/oil system, originally made by W. Lampe and E. Spicar

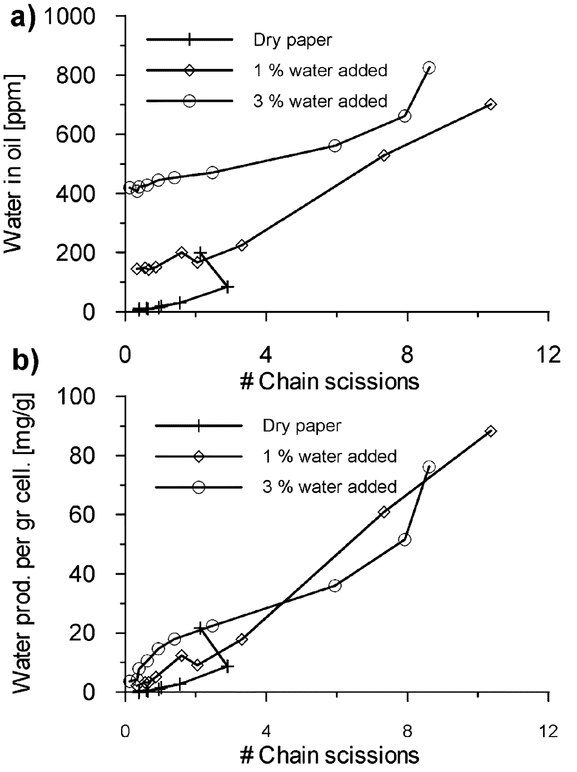

Fig. 9. Water production from the aging of Kraft at 130 °C: (a) moisture in oil; and (b) total water production.

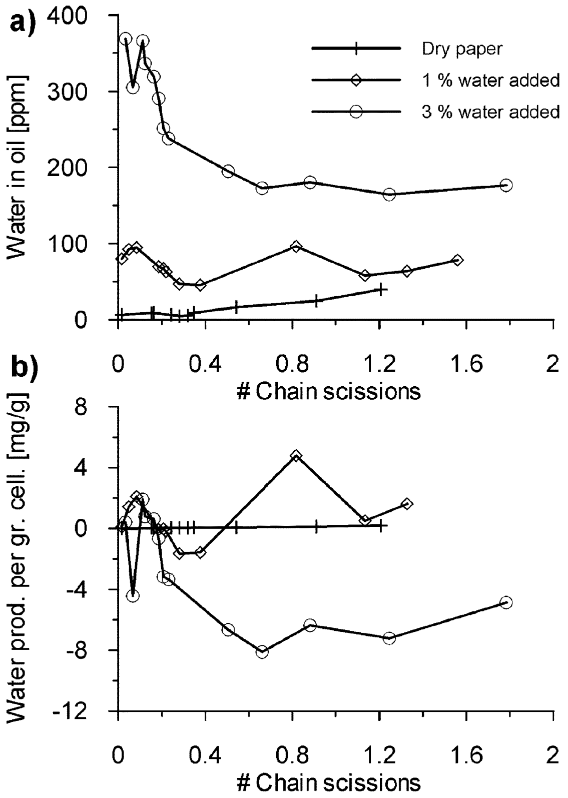

Fig. 10. Water production from aging of Insuldur at 130 °C: (a) moisture in oil; and (b) total water production.

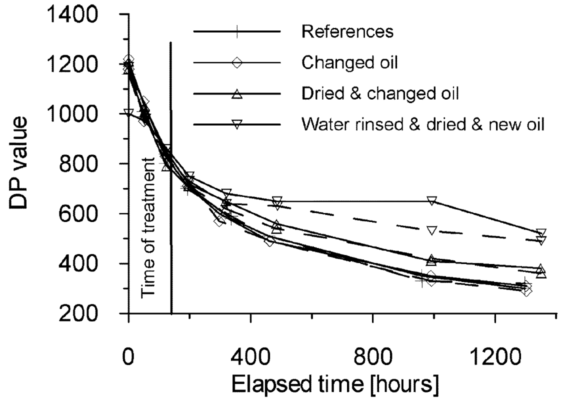

Fig. 11. Impact of reconditioning upon the aging of Kraft at 110 °C.

at ASEA and published in [7]. Fig. 9(a) shows how the water in the oil increased above the starting level as aging progressed. The total (calculated) water production is shown in Fig. 9(b).

For Insuldur, the situation was quite different, as shown in Fig. 10. The water content sometimes decreases. This is especially clear for the series in which water has been added. For clean and dry oil, and for the oxygenated oil, the water content grew slightly.

C. Attempted Reconditioning of the Paper

The results of these tests are shown in Fig. 11. The paper had an intial moisture content of 2.5%, and was aged to a DP of about 600. When the old oil was replaced by new and degassed oil, the humidity of the paper did not change. When the aged paper was dried *in vacuo* at 80°C, its water content was nearly halved, to 1.3%. When, however, the aged paper was washed in distilled water before drying, the same drying procedure reduced its water content to $<0.5\%$. Moreover, washing with water reduced the acidity of the paper more than drying only. It thus appeared that the aged paper contained nonvolatile substances that were both hygroscopic and acidic.

V. DISCUSSION

The basis for our treatment of the results is the observed, linear relationship between 1/DP and time within the DP range of practical interest (Fig. 4). The reaction rate later declines, notwithstanding the increases in water concentration and acidity. This paradox is readily explained by the much lower reactivity of the crystalline regions in the cellulosic fibrils [17], which would be expected progressively to compensate for the auto-acceleratory effect of the increasing acidity until, finally, they predominate and override it. This expected, compensatory effect evidently simplifies the analysis without invalidating it.

On average, our experimental results on Kraft paper confirm the findings of Emsley [10]. The activation energy was almost exactly as he proposed, and the acceleratory factor due to moisture also agrees well with his finding. We find that oxygen increases aging by a factor of about two, which also agrees with what Emsley later found [18]. We also found a similar value for the increase in water content per chain scission: about 0.5% [10]. However, a more detailed analysis of the results in Fig. 5(a) show that the temperature dependence is less for the oxygenated series than for those with water added: the series with water added showed an activation energy of 125 kJ/mole, while the

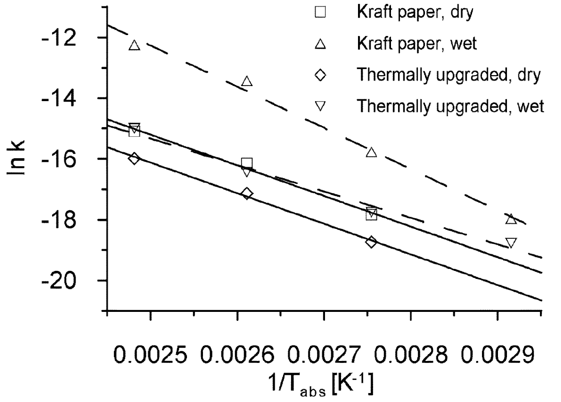

Fig. 12. Comparison between aging rates (k) of Kraft and Insuldur under both dry and moist conditions (3% water added to paper).

series with oxygen added showed an activation energy of 96 kJ/mole. In Fig. 12, Arrhenius plots are used to compare the aging of Kraft and Insuldur papers. Whereas the activation energies, indicated by the slopes, looks similar for dry paper of both types, the aging of Insuldur is slower by a factor of about three, and is less sensitive to added moisture.

Kraft and Insuldur also differ markedly in their production of 2FAL, acids and water during aging. Insuldur seems not to produce 2FAL at all [Fig. 6(b)]. It does, however, contain additives (dicyandiamide, melamine) whose primary amino-groups would react rapidly with any 2FAL (and related aldehydes such as 5-hydroxylmethyl-2-furaldehyde). This reaction has been well investigated because it occurs during the preservation of meat and fish by exposure to wood smoke [19], [20]. It belongs to a class of reactions known collectively as "the Maillard reaction" [21]. They occur between reducing sugars (and certain other aldehydes, including especially 2FAL and its derivatives) and primary amines of all kinds, including ammonia. They are strongly promoted by mildly acidic conditions, high temperatures, and low water activities. The end-product of any Maillard reaction is a dark brown, hydrophilic polymer called a "melanoidin." Melanoidins have antioxidant properties [21] and they also sequester multivalent metal cations, including especially those of iron and copper [20]. Superficially, they resemble the caramel that is produced by acid-catalyzed dehydration of hexoses in the absence of amines or ammonia, but they contain nitrogen and are therefore polyampholytes rather than polymeric acids. *It is a characteristic of all Maillard reactions that they lead to an increase in the acidity of the medium in which they occur.* In the first instance, this is due simply to the fact that ammonia and primary amines lose most of their basicity when they condense with aldehydes. Later, however, there is a net production of new, water-soluble, carboxylic acids [20], [21].

Whereas aging of Kraft produced water (Fig. 9), Insuldur rather consumed it (Fig. 10). On the other hand, Insuldur produced more acid than Kraft for a given number of chain scissions (Fig. 8). It is fundamentally unlikely that this additional acid arose from acid-catalyzed dehydration of the cellulosic chains in Insuldur, which would be the same as those in Kraft with the same number of chain scissions. We suggest therefore that the consumption of water and the production of additional acid by Insuldur are directly related as cause is to effect. One of the additives in Insuldur is stated by the manufacturers to be polyacrylamide, acid-hydrolysis of which would consume water with the release of polyacrylic acid and ammonia. Moreover, the carbohydrate chains carry cyanoethyl ether groups, hydrolysis of which would consume water with the production of acidic, carboxyethyl ether groups and ammonia. The ammonia would be consumed by Maillard reactions (not only with 2FAL but also with the reducing end-groups of cellulosic and hemicellulosic chains), and the acidity would increase.

It should be emphasized that the Maillard reaction takes place only with primary amines and ammonia. Secondary amines, such as dimethylamine, do form simple derivatives such as N-glycosides and amides, but tertiary amines such as triethylamine or TRIS (trishydroxymethylaminomethane, much used as a buffer in biochemical research) are unreactive with reducing sugars and aldehydes such as 2FAL. Quaternary ammonium ions such as cetyltrimethylammonium and cetylpyridinium (used in the antiseptics Cetavlon and Pyrisept, respectively) are likewise unreactive.

At first sight, the very low acceleration in aging brought about by an acidic, service-aged oil (Fig. 5) seems surprising. In this experiment, however, the paper contained only 0.5% of water, which was probably not enough to cause significant dissociation of the weak, carboxylic acids in the oil. Moreover, the fact that the neutralization value of the oil fell only a little (from 0.16 to 0.14 mg KOH/g) upon adding the paper suggests that very little of the fat-soluble acids in the oil had found their way into the paper. This result emphasizes the importance of distinguishing between the (mainly) hydrophobic acids that are produced by oxidizing the oil and hydrophilic ones such as formic acid, lævulinic acid, and caramel that are produced by the acid-catalyzed dehydration or the oxidation of cellulose and hemicellulose or from additives as detailed above. Ivanov has shown that more than 90% of the low-molecular formic and acetic acids added to a transformer oil is absorbed by paper impregnated with such an oil [22]. For a transformer in service, these would probably be water-soluble alkanoic acids such as acetic, propionic and butyric acids, and they would be selectively absorbed by the paper because the water concentration there is higher. This, too, is where their degree of dissociation would be the greater and their acidity higher.

These considerations suggest that a simple neutralization value for the oil alone is not a reliable guide as to the risks of accelerated paper aging. The neutralization values of both oil and paper should probably be measured both before and after water-extraction of the hydrophilic acids, since it is the latter that constitutes the greater risk factor. This conclusion is supported by the data in Fig. 11, which show that rinsing the paper with water gave the best reduction in aging rate. The paper was also easier to dry after extraction with water, thus proving that the hydrophilic acids help to bind water to the paper. This is most probably an effect of their osmotic pressure.

One should be aware that paper can contain contaminants; possibly including carboxylic acids. This is reflected in parameters such as dissipation factor and conductivity of aqueous extracts. In general, higher standards of cleanliness are upheld for papers that are used for capacitors and cables. Moreover, different oils age differently, and their aging products would be likely to influence the aging of the paper. Caution should therefore be exercised in generalizing upon the parameters reported here.

VI. PRACTICAL IMPLICATIONS

The utilities have several good reasons for wanting a qualitative and quantitative model for the aging of solid insulation materials in transformers. Such a model would:

- facilitate long-term planning for replacement of the older units;
- facilitate assessment of operational hazards such as uploading;
- provide a basis for cost-benefit analysis for maintenance and restoration.

The significance of water content is paramount: a humidity of 4% can shorten a transformer's operational lifetime by a factor of 40 (i.e., by 97.5%) while oxygen only reduces it to one-half. Fig. 13—based on an activation energy of 111 kJ/mole and A-values from Table II—shows calculated lifetimes for paper, starting with a DP of 1000 and ending its life when the DP has reached 200, according to the formula below

$$\text{Expected Life} = \frac{\frac{1}{DP_{\text{End}}} - \frac{1}{DP_{\text{Start}}}}{A{*}24{*}365} \cdot e^{(13350/T+273)}[\text{year}]. \tag{2}$$

Maintenance of the oil will not extend the service life of the cellulose unless aging accelerators like water, oxygen, and acids are removed from the *paper*. A simple reconditioning involving degassing and filtration of the oil will not do this efficiently enough. Oil is simply not a good extractant for the hydrophilic acids that accumulate in the cellulosic matrix of the paper, nor for the water that they help to retain there. One must therefore aim at drying the whole transformer, and not just its oil. Degassing at elevated temperatures might remove some water from the cellulose, but hot oil spray followed by vacuum drying or vapor-phase processing are more efficient drying methods [23]. Spraying with hot oil may be less efficient for parts that are not directly exposed to the spray [24], but heating the windings by, for example, a low-frequency current may compensate for this.

Oil reclaiming using, for example, Fullers earth, usually combined with a reconditioning process, is an efficient way of removing acids and other byproducts from aging such as aldehydes and ketones. If the filtration is repeated several times, a good, long-term stability in the oil's acid number is reported [25], but it is not clear how far this also removes acids from the paper. As long as most of the water remains with the cellulose, one may suspect that most of the low-molecular, hydrophilic will remain there too. Hot-oil spray and vapor-phase processing may, however, evaporate and remove acids of low boiling point (such as formic acid) from the cellulose.

The required drying time for a transformer depends upon the concentration of moisture in the cellulose, which is usually estimated indirectly from its concentration in the oil with the help of equilibrium data [7]. There are, however, uncertainties inherent in this procedure, especially those arising from the fact that the temperature inside a transformer is not uniform.

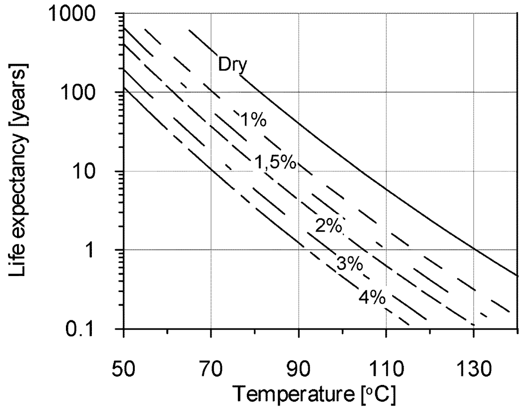

Fig. 13. Expected life for solid insulation and its dependence upon moisture and temperature.

It is natural to assume that a transformer should be dried as rigorously as possible. When, however, the water content has increased slowly over a long period of time, the cellulose swells and to some extent undergoes a plastic deformation. During subsequent drying, the paper and pressboard in the winding will shrink, and the transformer may end up with a reduced clamping pressure and a loose winding. Hence, the drying should only be partial unless it is possible to reclamp the winding.

A consideration of the accepted mechanisms of oxidation [14] and acid-catalyzed hydrolysis [11],[12] suggests that deterioration of the paper must begin with oxidation, when its moisture content is low and free from acidity. Oxidation in both oil and paper produces acidity, which progressively suppresses further oxidation, while initiating acid-catalyzed hydrolysis and dehydration reactions. The latter produce additional acids nonoxidatively, and also water, which increases the catalytic efficiency of the acids by promoting their dissociation. Expressed in other terms, oxidation is auto-inhibitory and acid-catalyzed degradation is auto-acceleratory.

In summary, aging of cellulosic insulation in transformers is caused by oxidation, carboxylic acids, and water, which enhance the catalytic efficiency of the acids by promoting their dissociation. In theory, aging could be prevented by excluding oxygen completely from the system [17], but this is only relevant for new transformers with low concentrations of carboxylic acids and water. A second line of defense would be to remove the water and the acids continuously from the system as they are formed. It is relatively easy to remove them from the oil, and since the oil and paper are expected to be in some sort of equilibrium, it may be assumed that reconditioning the oil would automatically recondition the paper. Our findings do not, however, encourage the belief that this would be an efficient procedure. Equipment for continuous drying of the oil incorporating cold traps or vacuum extraction is commercially available. Once again, these techniques are best suited for new transformers because of the danger of shrinkage upon drying a wet insulation. One also needs to check the effect of a continuous degassing on diagnostic measurement and analyses of dissolved gases from defects and aging of oil and cellulose before such measurements can be recommended.

Insuldur has performed impressively in this investigation. It contains additives, which consume water by reacting chemically with it, and organic bases which partly neutralize the acids. This increases its lifetime by a factor of about three, compared to Kraft. On the other hand, it also produces more acid than Kraft. We have suggested that these additional acids originate more from some of the additives than from the paper, and that Insuldur's performance could be enhanced still further by changing some of the additives so as to make them less reactive with aldehydes and other carbonyl compounds.

VII. CONCLUSION

- Our results confirm the validity of models and parameters proposed earlier for the aging kinetics of Kraft paper and the influence of water and oxygen.
- A refined model is proposed that recognizes the effect of water in enhancing the catalytic efficiency of the acids produced during the aging of Kraft paper.
- The activation energy (temperature dependence) for the aging of Insuldur upgraded paper seems to be the same as that for Kraft paper.
- Aging of the paper also increases the acidity of the oil.
- Insuldur upgraded paper does not produce as much 2FAL as Kraft paper and, hence, 2FAL cannot be used as an index of aging in papers of all types.
- Water is more important than oxygen for transformer aging, because dry acids have little catalytic efficiency.
- Acids are of central significance for understanding the aging of paper and for evaluating the effects of oil maintenance.

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