Study Committee D1

Materials and Emerging Test Techniques

Paper D1-PS1-10982

Differences in ageing pattern and production/consumption of ageing markers in kraft and thermally upgraded papers immersed in mineral and natural ester oil

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Motivation

- Today, there is no unique, standardized procedure for testing the quality of thermally upgraded papers (TU) in order to compare their capability.
- New test methods for the evaluation of paper ageing are going to be investigated within the new CIGRE WG D1.76: "Tests for verification of quality and ageing performance of cellulose insulation for power transformers".
- **Comparative study of ageing of TU and Kraft paper in mineral oil and natural ester oil** was performed **in order to get more insight in the differences in degradation patern of different insulation systems.**

Method/Approach

- This paper studied the **ageing of different standard thermally upgraded papers (TU), normal Kraft paper, and novel upgraded paper (NTU) in mineral and natural ester oil at 170 °C**.
- **Ageing markers**, carbon dioxide, methanol, and furans **were** also **monitored** in order to compare their appearance in different oils with different types of insulating papers.
- **The dissolution & stability of ageing markers** in the oil were investigated by heating the ester oil spiked with methanol/2-furfural.
- **Differences in ageing kintetics of one standard TU paper and NTU paper** were investigated by ageing **at 160°C, 170°C and 185°C.**
- **The impact of water produced** during ageing of paper **on paper degradation rate was investigated** throughout **ageing in cycles** and in vessel with higher tightness **at 185 °C** .

Objects of investigation

- Normal kraft paper, 5 standard TU papers (TU1, TU2, TU3, TU4, TU5) and novel TU paper (NTU) were aged in 10% mass to the mass of oil.
- Two types of oil were used: naphtenic, inhibited, high grade mineral oil and natural ester (triester) inhibited oil.

Figure 1. Ageing vessels: aluminium bottle (left), closed erlenmayer flasks (middle), head space vials (right)

Experimental setup & test results

- Dried and impregnated insulating papers were aged with mineral and ester oil at 160°C, 170°C, and 185°C for 120 days, 32 to 60 days, and 18 days respectively.
- Experiments were performed in glass erlenmayer flasks closed with stopper, purged with Nitrogen before ageing.
- Tests performed during ageing are: DGA acc. to IEC 60567, methanol and ethanol content acc. to IEC TR 63025 (integrated TOGA GC FID method), oil acidity acc. to IEC 62021-1 and IEC 62021-2, furans acc. to IEC 61198, water content in the paper acc. to IEC 60814 and DPv of the paper acc. to IEC 60450.
- Impact of produced water on ageing and dissolution & stability of aging markers in the oil were investigated in Aluminium bottles with a threaded lid and PFTE O-ring and in head space vials with PFTE septa.

Discussion

- **Paper composition had a significant impact on thermal performance of papers during ageing**, while oils were observed not to modify papers ageing rates significantly.
- **Methanol was consumed in reaction with fatty acids**, while **furans were found to be less soluble in the natural ester oil**, possibly owing to stronger intermolecular bonding of esters to cellulose free hydroxyl groups.
- **Water resorption-migration from the headspace and oil back to the paper** was observed during ageing in cycles and **had stronger impact on paper aging rate in case of mineral oil.**

Conclusion

- Results obtained in this study and comparison to previous research showed that **modification of ageing conditions** and change of ageing mechanism from hydrolysis to pyrolysis with increase of aging temperatures **may lead to different life estimations of the same and different paper/oil insulation systems.**
- **Concentrations of ageing markers and their ratios are strongly dependent on the composition of the paper and the type of oil.**
- **Accelerated ageing tests of insulating papers should be used for comparison of materials quality and not to simulate ageing performance of real systems**.

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Comparison of insulating papers ageing in mineral and natural ester oil

- **Ageing of Kraft paper was significantly faster** in comparison to TU papers **at 170 °C in mineral oil and natural ester oil.**
- Differences among TU papers remained of the same order until the end of ageing.
- **NTU paper reached longest duration until end of life** (DPv = 200) among investigated TU papers.

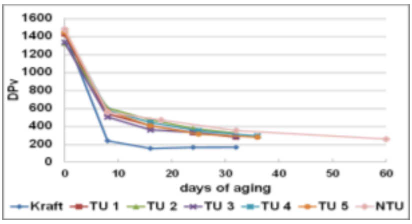

Figure 2a. Change of DPv with time in six TU and one Kraft paper at 170°C in mineral oil

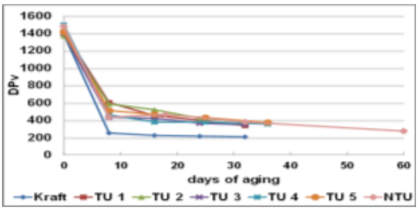

Figure 2b. Change of DPv with time in six TU and one Kraft paper at 170°C in natural ester oil

TU 1 paper and NTU paper thermal class

- **Ageing of TU1 and NTU papers in mineral and natural ester oil** was performed at three temperatures: **160°C, 170°C and 185 °C** in order to compare their ageing kinetic and thermal classes.
- Thermal class of **TU 1 paper was 130 °C in both oils**, while **NTU paper obtained thermal class 140°C in natural ester and 130 °C in mineral oil** (calculations were made in the manner of IEC 62332-2).

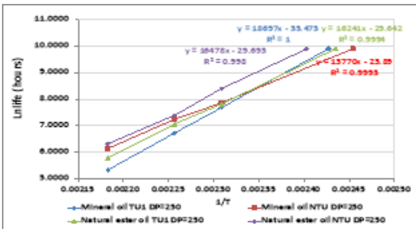

Figure 3. Life curves of TU1 and NTU

TU 1 paper and NTU paper ageing kinetics and mechanism

- Kinetic parameters have shown much **weaker performance of TU 1 paper in mineral oil in comparison to NTU paper**, while in natural ester oil were found to be **very similar for both TU papers.**
- Obtained activation energies correlated well to published values in similar temperature range of TU papers ageing (150 -190°C).
- **In these specific conditions** (low water and oxygen and absence of metal catalysts) **paper ageing rates were not very much influenced by the oil type** (mineral and natural ester oil).

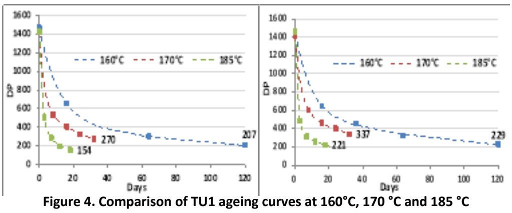

Figure 4. Comparison of TU1 ageing curves at 160°C, 170 °C and 185 °C in mineral (left) and ester oil (right)

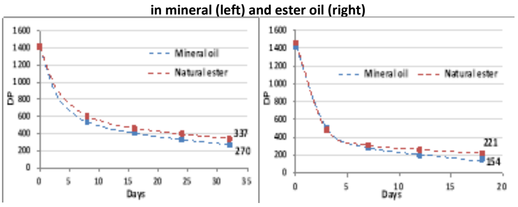

Figure 5. Comparison of TU1 ageing curves in mineral and natural ester oil at 170°C (left) and 185°C (right)

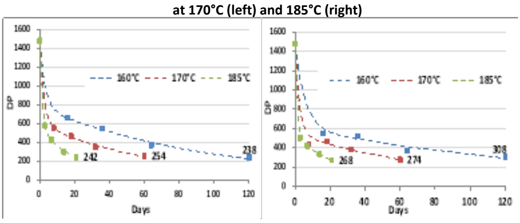

Figure 6. Comparison of NTU ageing curves at 160°C, 170 °C and 185 °C in mineral (left) and ester oil (right)

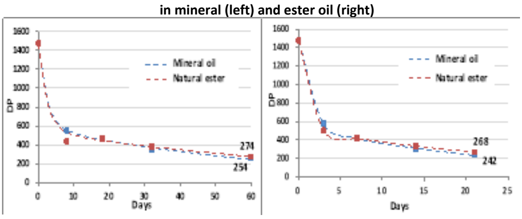

Figure 7. Comparison of NTU ageing curves at 170°C (left) and 185°C (right) in mineral and natural ester oil

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Oil ageing markers

- Paper ageing markers trends were investigated **at 170°C**
- **Furans concentrations in TU papers were 20-30 times lower in both oils,** possibly due to their reaction with Nitrogen compounds in the paper.
- **Furans and methanol** (MetOH) were detected **in significantly lower concentrations in natural ester oil** in comparison to mineral oil.
- **Carbon dioxide** (CO_2) **was produced in much higher amounts in natural ester oil than in mineral oil**. Significant fluctuations of carbon dioxide during paper ageing was observed.
- Trends of CO_2 and methanol mostly matched in both oils.
- **Acid content** (Nb) **in natural ester oil was around ten times higher** than in mineral oil.

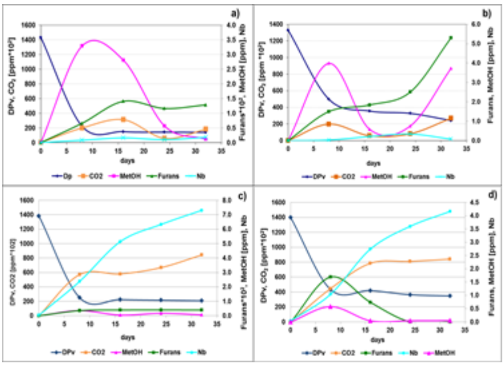

Figure 8. Correlations of DPv to ageing markers in the oil: a) kraft paper in mineral oil, b) TU3 paper in mineral oil, c) kraft paper in natural ester oil, d) TU3 paper in natural ester oil

Impact of generated water on paper ageing rates/ Ageing in cycles

- Experiments were conducted in aluminium bottles at 185 °C in three cycles for 6 days each with cooling for 24 h and resting at ambient temperature 48h.
- **Water increase in the paper at the end of** ageing in **three cycles was observed and was more pronounced** in the system **with mineral oil.**
- Small increase of paper ageing rate was observed in the case of mineral oil.

Table 1. Results of TU 1 aging closed system with MO and NE at 185°C

Properties	MO 18 days	MO 3x6 days	NE 18 days	NE 3x6 days
Water content in the paper - initial, %	0.07	0.27	0.11	0.09
Water content in the paper - end, %	1.47	2.3	0.16	0.38
Oil acidity - initial, mgKOH/g	0.00	0.00	0.05	0.05
Oil acidity – end, mgKOH/g	0.06	0.11	9.2	11.26
Paper DPv, end	156	142	229	233

Ageing of natural ester oils spiked with methanol and furans

- **New (dry and wet) and aged natural ester oil were heated at 170°C for 72 h** in two types of vessels: Aluminium bottle (Al bottle) and glass vials with PFTE septa **with added methanol/2-furfural.**
- **Methanol was consumed** in reactions with natural ester oil and to a much higher extent in aged oil. Consumption was also more pronounced in wet ester oil.
- **Furans were stable** in the oil during heating experiments. This revealed that low furan values in ester oils were consequence of their restricted dissolution in ester oil.

Table 2. Ageing of natural ester oils at 170°C for 72 h, spiked with methanol and furans

Natural ester oil spiked with methanol				
Oil		Water content in oil, ppm	Methanol, ppb	Acidity, mgKOH/goil
Aged	Initial	81/121*	3364/3180*	3.00
	Al bottle	83	33	2.79
	Vials PFTE	45	16	3.12
New	Initial	50	2453	/
	Al bottle	73	1557	/
	Vials PFTE	108	1422	/
New and Wet	Initial	508	2588	/
	Al bottle	/	/	/
	Vials PFTE	416	1115	/

Natural ester oil spiked with furans					
Oil		Water content in oil, ppm	Methanol, ppb	Acidity, mgKOH/goil	Furans, ppm
Aged	Initial	147	16	3.10	12.88
	Vials PFTE	55	15	3.29	9.10
New	Initial	93	24	0.21	10.00
	Vials PFTE	238	13	0.66	10.48
New and Wet	Initial	670	14	0.21	10.41
	Vials PFTE	319	3	1.79	9.51

Conclusion

- Kraft paper aged much faster in comparison to thermally upgraded papers.
- Novel TU paper reached longest duration until end of life among investigated TU papers.
- Difference in thermal class between paper immersed in mineral and natural ester oil were at the most 10°C in the case of novel TU paper. Small differences in papers ageing in mineral and natural ester oil was owed to dry and low oxygen ageing conditions.
- Kinetic parameters were similar for two investigated TU papers aged in natural ester oil, while in mineral oil differences were observed and probably were caused by the change of dominant ageing mechanism.
- Higher acidity of natural ester oil did not have a strong effect on paper degradation rate compared to mineral oil .