Changes in Mechanical Properties of Impregnated Nomex Papers 410 and 910 During Accelerated Aging

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Abstract

New materials are currently being developed for applications in transformer design. With the useful life of transformers now determined by solid insulation conditions, a better understanding of aging kinetics is important in order to improve electrical system management and planning from the technical and economic points of view. This paper summarizes an investigation of the effects of impregnating aramid and cellulose/aramid papers (Nomex 410 and 910) with insulation fluids (Nynas Polaris and Luminol Tri) at thermally accelerated conditions (170°C) on their mechanical properties.

It was found that Nomex 410 (100% aramid) showed only a small change in tensile strength (~5% decrease) after accelerated aging (around 7,500 hours). However, its elongation capacity was significantly reduced (~45-70% decrease for dry and wet Nomex 410, respectively) by the end of the aging process, probably due to hydrolysis. In addition, the interaction between water and aramid hydrogen bonds at high temperatures produced the rupture and then, the randomly rebuilt of these bonds in meta-aramid fibres, thereby reducing its plastic deformation capacity.

In the case of Nomex 910 (aramid enhanced cellulose), its mechanical properties were maintained for a longer time than those of thermally upgraded Kraft paper (TUK), as measured by the retained percentage of tensile index. However, when the tensile index was used instead of the retained percentage, TUK showed a higher tensile index value than Nomex 910 during the initial stage, while the values for both papers became similar during the second stage. It is only at the end of the aging process that Nomex 910 presented an advantage over TUK paper due to the addition of the aramid fibres.

It was also found that the inception fractures in Nomex 910, as a fibrous layered composite paper, start in the weakest part of the composite, probably in the central cellulose layer. The fracture line follows the weakest path, avoiding the aramid fibres.

The results presented in this paper can be used as a benchmark for improving our understanding of aging and changes in the mechanical properties of these relatively new materials used in the solid insulation of power transformers. A better understanding of the aging characteristics (thermal degradation) of aramid-based papers should help better assess the condition of the new generation of power transformer fleets.

Keywords. - Nomex 410, Nomex 910, aramid, cellulosic insulation, power transformer, solid insulation

1. Introduction

For more than 100 years, cellulose fibre paper has been used as solid insulation in power transformers due to its good dielectric and mechanical properties. The aging/degradation mechanisms of cellulose paper are still studied as a means of determining the remaining service life of power transformers. The relationship between changes in the mechanical properties of paper and the chemical markers of aging has been investigated for this purpose [1-3].

As the global demand for energy increases every year, so does the demand for higher-capacity transformer units. Thus, enhanced solid insulation materials are gradually being introduced for use in the next generation of transformers.

Paper based on 100% aramid fibres (e.g., Nomex 410) is a fairly new solid insulation used in power transformers. The thermal class of Nomex 410 (220°C) exceeds that of Kraft (105°C) and TUK papers (120°C). To narrow the gap between the aramid thermal class and the thermal classes of cellulose papers, a composite fibrous material (e.g., Nomex 910) was developed by DuPont in 2014 [4]. This composite paper material is based on cellulose fibres reinforced with aramid fibres, and has a better thermal class than TUK paper (130°C) [4, 5] and a lower price than 100% aramid paper [5]. With this aramid-enhanced cellulose paper, power transformer loading capacity is also increased by 10% over that of power transformers with TUK paper [5].

Nomex 410 and Nomex 910 are used in power and distribution transformers due to their good mechanical properties and high heat resistance. However, little is known about changes in their mechanical properties and their aging mechanisms during service life.

1.1 Aramid fibres for insulation paper

Aramid is produced by a polycondensation reaction [6] consisting of benzene ring joints in alternation with amide groups along its chain axis [7]. The molecular chains of aramid are linked by strong covalent bonds (intramolecular hydrogen bonds) [7]. The aramid chains exhibit a high degree of fibre orientation due to their chemical structure (a radial pleated structure aligned along the fibre axis) [8-12].

Due to their very stable chemical structure and strong intramolecular bonds, the aramid fibres have high values for thermal stability, longitudinal tensile strength, Young's modulus, elasticity and flexibility, even when splitting or delamination occur [7-9, 12]. However, in the cross-radial direction, its transversal tensile strength and shear strength are low because the chains are radially linked by weaker hydrogen bonds [8, 12, 13].

Aramid paper is manufactured using mainly meta-aramid fibres. An organic carbon-based partially oriented crystal liquid is spun (extruded), washed and dried to form high-oriented meta-aramid fibres [8]. The meta-aramid fibres have a cylindrical shape. In cross section, they have a dumbbell or dog-bone shape. Their density is 1.38 g/cm^3 [14] and their water content can reach values of around 5% at 65% relative humidity and 20°C [11, 14].

1.2 Degradation of meta-aramid fibres

The degradation of meta-aramid fibres by pyrolysis was studied under an argon atmosphere at temperatures up to 900°C. The analysis showed scission of hydrogen bonds at the 300–400°C range and

two marked weight losses (one related to the release of moisture in the fibres, and the second to the release of water molecules from the scission of the hydrogen bonds) [15].

Aramid is also partially reactive to hydrolysis. The hydrolysis reaction, using water contained in the fibres, causes a loss of mechanical properties and thermal stability. The presence of water also breaks the intramolecular hydrogen bonds inside the aramid fibres. At the same time, random hydrogen bonds form between the meta-aramid fibres [16]. At high relative humidity (higher than 10%), aramid also shows limited resistance to hydrolysis [14].

1.3 Components of aramid papers

The structural components of aramid paper are flocs and fibrids, both of which have the same composition [7]. Aramid flocs are short sections of long aramid fibres [6] that are approximately 6 mm in length and 10 µm in diameter and have a rigid tube shape [7]. Aramid fibrids have a flexible, irregular fibre-film form and are 0.2–1 mm long and less than 1 µm thick [7]. The fibrids act as binders, keeping the aramid fibres together. They also work as fillers in aramid paper [7]. Hydrogen and Van der Waals forces are formed among aramid fibres (interfibre) and between aramid fibrids and aramid fibres [7]. The adhesive force between fibres and fibrids is five times weaker than the fibrid-fibrid force. This is due to the larger contact area in the case of fibrids [7].

1.4 Nomex 410 and 910

The manufacture of aramid papers is similar to the conventional wet-paper-making process, with a few additional steps [6, 7]. The aramid fibres and fibrids are soaked in water to produce a well-dispersed suspension, an aramid pulp slurry. The aramid slurry is then mixed with short aramid fibres to form a paper pulp. The fibres are produced by the fibrillation and cutting of spun fibres. However, in other cases, the fibres are produced directly without the spinning process [6, 17]. Next, the wet aramid paper pulp goes through the papermaking process: lamination (wet paper sheets), pressing (dewatering and drying) and calendering (paper sheets) [6, 7, 17].

The mechanical strength of aramid paper is directly related to the length of the aramid fibres and the paper's degree of uniformity (fibre dispersion and orientation) [6]. An ultrasonic wave generator is used in the manufacture of aramid papers to improve fibre dispersion, increase the degree of horizontal orientation of the aramid fibres and reduce the degree of their vertical orientation [6, 17].

Nomex 410 is a single-layer paper made with aramid flocs/fibrids in equal proportion. Depending on the application, however, the fibre/film ratio may vary. A higher percentage of fibres improves oil impregnation. Nomex 410 is less hygroscopic than cellulose paper at the same conditions [18].

Nomex 910 is an aramid-enhanced cellulose paper. It is made with cellulose (approx. 70%), thermally upgraded Kraft pulp and meta-aramid fibres (approx. 30%) [4]. It is composed of three layers, pressed to form a single layer. The two outer layers are a mix of cellulose and aramid fibres [4, 19]. The central layer is pure cellulose fibres (TUK). The cellulose fibres provide mechanical support for the paper [4, 19]. The aramid fibres improve the mechanical support and thermal stability of the cellulose fibres [4].

2. Materials and Methods

2.1 Materials, sample conditioning and aging cell preparation

Two types of insulation fluids were used: a mineral oil, Nytro Polaris GX (Polaris) made by Nynas is an inhibited oil and fulfils the requirements for CAN/CSA- C50-14 (Class A Type II) and ASTM D3487 (Type II) and an inhibited synthesized fluid, Luminol TR-I (Luminol), made by Petro-Canada. Luminol meets the requirements of CAN/CSA C50 (Class A Type II and IV) and ASTM D3487 (Type II). In addition, four types of paper were used: Kraft paper (Kraft), thermally upgraded Kraft paper (TUK), Nomex 910 and Nomex 410. The physical properties of the insulation fluids and papers are presented in Tables 1 and 2.

Hermetic stainless steel aging cells were used to partially simulate a sealed power transformer. Thirteen bands of paper (25.4 mm x 130 mm) in a copper sample support structure, to avoid paper folds, and 230 ml of insulation fluid were placed in each aging cell.

Oil and paper were conditioned for at least one week in a double glove box in dry air with 0.9% relative humidity. The only exception was a set of Nomex 410 samples, which were used in laboratory conditions (air atmosphere at 31% RH and 20°C). The initial water content of the papers was measured at the end of the equilibrium process (see Table 1). The aging cells were hermetically closed inside the glove box to maintain the initial conditions. A detailed description of the aging cells, equipment and procedures can be found elsewhere [20]. The aging cells were placed inside air-forced ovens (Salvis lab, type TC-100S) at 170°C. This temperature was selected to allow for observation of aging effects in a short time and comparison with the results of previous studies.

Nomex 410 was studied in two initial water content versions in order to show the effect of aramid moisture content on aging mechanisms. The Nomex 910 paper was impregnated with two types of oil to compare the effect of the type of oil on paper aging. The following nomenclature (see Table 3) was used to identify the various samples and conditions.

Table 1. Physical Properties of the Studied Papers

Name	**Kraft (5A2-1H1)**	**Kraft TUK (Insuldur)**	**Nomex 410**	**Nomex 910**
Manufacturer	**Munksjö AB**	**Weidmann AG**	**DuPont**	**DuPont**
Grammage (g/m^2)	40	63	64	80
Thickness (µm)	50	75	76.2	76.2
N_2 (%)	0.04	2.6	N/A	N/A
H_2O (%)	1.25	0.96	0.7 / 2.9	0.78
$DP_{v,o}$ (Initial DPv)	1,222	1048	N/A	1273 **[*]**
Initial Tidx (N.m/g) MD	127	183	109	88
Initial Tidx (N.m/g) XD	N/A	N/A	54	19

[*] Measured on the cellulose part. MD: machine direction, XD: cross direction

Table 2. Properties of insulation fluids

	Units	Nynas Nytro Polaris GX	Petro-Canada Luminol TRi
PHYSICAL PROPERTIES			
Density at 15°C	g/mL	0,906	0,83
Kinematic viscosity @ 100°C	mm^2/s	1,9	2,8
Kinematic viscosity @ 40°C	mm^2/s	7,5	9,2
Kinematic viscosity @ 0°C	mm^2/s	44	53
Kinematic viscosity @ -40°C	mm^2/s	2000	1230
Flash point	°C	145	170
Pour point	°C	-46	-65
Interfacial tension @ 25°C	mN/m	48	48
CHEMICAL PROPERTIES			
Acidity	mg KOH/g	< 0.003	<0.01
Initial water content	ppm	<20	<20
PCB content	ppm	nil	nil
Corrosive Sulphur		not corrosive	not corrosive
Inhibitor content	wt.%	0.3	0.2
ELECTRICAL PROPERTIES			
Breakdown voltage	kV	>40	55
Gassing tendency	µl/min	negative	-10

Table 3. Nomenclature and Description of Samples

Sample Name	Description
Nomex 410 0.7%w-Pol	Nomex 410, initial water content of 0.7%, Nynas Polaris oil (dry Nomex 410)
Nomex 410 2.9%w-Pol	Nomex 410, initial water content of 2.9%, Nynas Polaris oil (wet Nomex 410)
Nomex 910 0.8%w-Pol	Nomex 910, initial water content of 0.8%, Nynas Polaris oil
Nomex 910 0.8%w-Lum	Nomex 910, initial water content of 0.8%, Luminol Tri
Kraft 1.2%w-Lum	Kraft paper, initial water content of 1.2%, Luminol Tri
TUK 2.6%N 1%w-Lum	TUK paper with 2.6% of N, initial water content of 1%, Luminol Tri

N%: nitrogen content by weight

2.2 Analysis techniques

The tensile index of paper was measured based on ASTM Standard D828. The measurements were performed using a tensile machine (Testing Machine Inc., Series 84-76). The accuracy of the tensile machine declared by the manufacture is ±0.5% of reading. Thirteen paper specimens per study point were used. A total of 13 samples were cut in the machine direction (MD) for the Kraft and TUK papers, while 7 samples were cut in the MD and 6 in the cross direction (XD) for the Nomex 410 and 910 papers, respectively. The value used was the mean of each data set with its respective standard deviation.

Paper water content was measured by dry methanol extraction followed by Karl Fischer titration in accordance with ASTM D 1348. The degree of polymerization (DP_v) of the cellulose papers (Kraft and TUK) was calculated using the average intrinsic viscosity value based on ASTM Standard D4243. The average value of the two measurements was used as a point of reference. For Nomex 910, the DP_v of the cellulose

component was measured using a similar method, with some additional steps. The Nomex 910 samples' weight was higher (around 40%) than that of the Kraft and TUK papers in order to compensate for the aramid component. After the Nomex 910 sample was dissolved in cupri-ethylene-diamine, the solution was filtered using a Büchner funnel. The dried non-soluble part (aramid) was weighed, and the quantity of cellulose in the sample was estimated by weight difference. Subsequently, the same steps as for Kraft and TUK papers were followed. The DP_v of Nomex 410 was not measured.

The morphology of the aged Nomex 910 and 410 papers was observed on SEM micrographs (Hitachi 3500 SEM operated at 15keV equipped with an X-Max electron dispersive spectroscopy (EDS) detector (Oxford Instruments)) and using an infrared microscope (Nicolet iN 10, Thermo Scientific). The fracture zone and type of fracture of the Nomex 910 and 410 were analyzed using a stereomicroscope (Stemi 2000-CS, Carl Zeiss, Germany).

3. Results and discussion

3.1 Mechanical properties

Figure 1 shows the variation in retained percentage of the initial tensile index (Tidx) in the machine direction for the Nomex 410, Nomex 910, Kraft and TUK papers. The Kraft and TUK values were obtained from our previous study [1] and included for comparison purposes.

Kraft paper exhibits the fastest loss of tensile strength in the group (in less than 1000 hours). TUK paper performance is superior to that of Kraft paper and shows a slower rate of decrease in tensile strength (around 65% lower, using as reference 10% of retained Tidx) due to the addition of nitrogen additives to its cellulose matrix. Since acid hydrolysis is the main ageing mechanism of cellulose paper degradation, the presence of stabilizing additives (amides salts) neutralize the acids that are formed during ageing of cellulose and oil and slows down the depolymerization and the decrease of tensile strength. However, TUK paper performance is inferior to that of the Nomex papers.

In the case of Nomex 410, regardless of its initial water content (dry and wet), its retained percentage of Tidx did not decrease during the first stage of the aging process (first 4,000 hours). A slight increase (~ 5%) in the retained percentage of Tidx of Nomex 410 (dry and wet) was detected within the first 500 hours, probably due to the annealing process. Annealing should enhance the crystalline structure and release the internal stress of the aramid fibres. In the second stage of aging, between 4,000 hours and the end of aging, only Nomex 410 with an initial 2.9% water content (wet Nomex 410) showed a decrease of almost 20% in its initial tensile index. The higher initial water content in wet Nomex 410 affects the mechanical properties of the aramid fibres by breaking the original aramid interfibre hydrogen bonds and randomly forming new ones [16].

Nomex 910 shows better mechanical performance than Kraft and TUK. Nomex 910's mechanical strength decreased significantly more (~40% loss of retained Tidx) than that of Nomex 410 during the first 1,000 hours. This initially faster decrease in tensile strength is related to the scission of 1,4-b-glycosidic bonds, mainly in the amorphous regions of cellulose by acid hydrolysis [21]. The depolymerization of cellulose chains triggers different mechanisms that result in the loss of Nomex 910's mechanical properties [1]. At a subsequent aging stage (1,000-2,000 hours), a ~ 50% of decrease in the tensile strength of Nomex 910 was observed. This was probably due to slow cellulose depolymerization in Nomex 910. At the end of the aging process (2000 hours to the end), cellulose depolymerization continued, but at a slower pace (~40%

of initial rate). The addition of aramid fibres does not appear to stop or slow the effect of acid hydrolysis on the cellulose component. The aging behaviour of Nomex 910 is independent of the impregnating oil used. The use of Luminol TRi, a highly stable oil against oxidation, does not offer any advantage over Nynas Polaris, a regular mineral oil, in slowing down the degradation of Nomex 910. As explained in a previous work [22], this is probably due to the fact that some of the degradation species generated by insulation fluid aging (water, acids, etc.) are retained in the aramid layers and neutralized/consumed by the nitrogen additives (TUK-cellulose). This barrier effect minimizes the impact of using a stable fluid against oxidation.

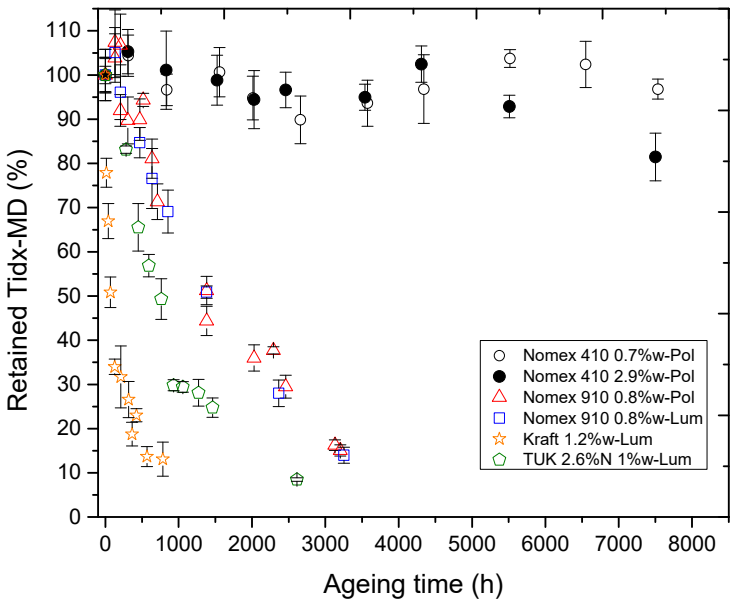

Figure 1: Retained initial tensile index percentage in the machine direction for Nomex 410, Nomex 910, Kraft and TUK papers at various initial water contents impregnated with Nynas Polaris (Pol) or Luminol Tri (Lum)

In cellulose-based paper, some sections have a lower tensile strength than the nominal value due to manufacturing defects (curls, kinks, micro-compressions, etc.), low paper uniformity and poor alignment of discontinuous fibres [23]. Thus, the mechanical strength of cellulose-based paper is determined by the strength of these weak zones. The same should apply to Nomex 910 due to its cellulose component. This also explains the large standard deviation in the tensile index values of these materials.

Based on the results, it could be inferred that fracture initiation in Nomex 910 should occur in weaker areas, likely in the central cellulose layer. In addition, fracture propagation likely follows a less resilient path through cellulose fibres and avoiding aramid fibres (Figure 2).

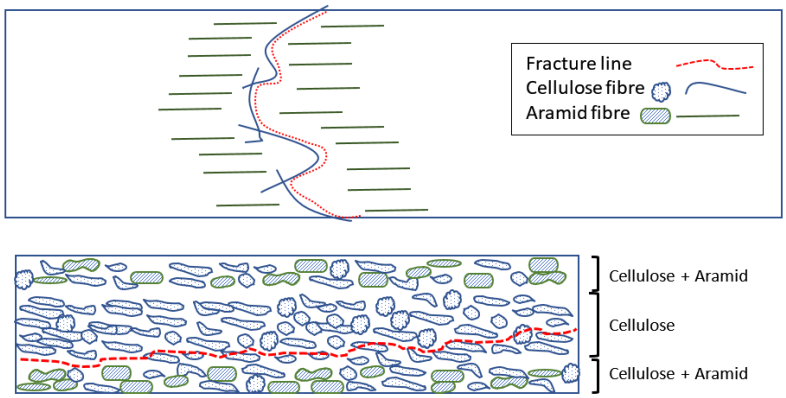

Figure 2: Schematic drawing of longitudinal and cross-section views of Nomex 910 showing a probable fracture path under tensile force

Figure 3 shows the papers' tensile index values (Tidx) rather than their retained percentages of initial tensile index, as in Figure 2. These initial tensile index values are around 88–127 N.m/g for most of the papers (see Table 1). The exception is TUK paper, at 183 N.m/g. The Tidx for TUK paper is higher (67%-107% more) than for Nomex 410 and 910. Kraft paper performs poorly in comparison with the other papers. As in Figure 1, it again shows the fastest Tidx decline in the group (reaching a value of 20N.m/g in less than 1000 hours). In the case of Nomex 410 (wet and dry), its Tidx remains almost stable for a longer time than other types of paper. However, as shown in Figure 1, wet Nomex 410 shows a loss of Tidx at the end of aging.

In the case of TUK and Nomex 910 papers, TUK paper exhibits a faster loss (~ 25% than Nomex 910 using the end of aging as reference) of tensile strength than the Nomex papers. However, it also shows a higher tensile index value than the Nomex papers during the first 500 hours. This advantage should last longer at lower temperatures. Between 500 and 750 hours, the TUK paper degradation rate slows and its tensile index values are lower (~5-20N.m/g) than for Nomex 410, but higher (~25 N.n/g) than for Nomex 910. Between 750 and 2,000 hours, the Tidx of TUK paper and Nomex 910 showed similar values and degradation rates. At the end of aging, TUK paper and Nomex 910 are very brittle and fragile materials. Nomex 910 shows a slower rate of tensile index decrease than TUK paper. The final Tidx values were 13N.m/g (15% of the initial value) after 3,200 hours for Nomex 910, and 15.5 N.m/g (8% of the initial value) after 2,600 hours for TUK paper.

In the case of Nomex 910, the addition of aramid fibres to its cellulose matrix gives it a longer service life than TUK paper. However, this improvement occurs in the final phase of aging (2,500–3,200 hours). The improvement may be more effective if the Nomex 910 central layer also contains aramid fibres, with the associated higher cost. Based on the results, it can be assumed that Nomex 910 performs more like TUK paper than Nomex 410.

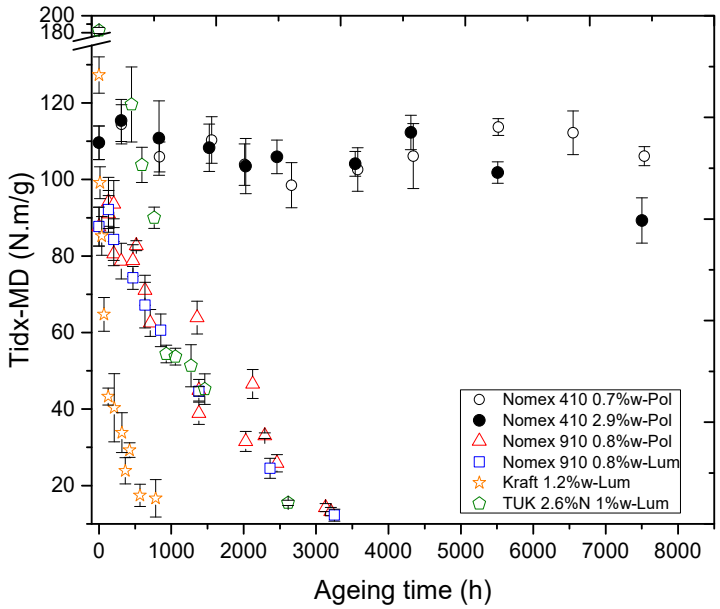

Figure 3: Tensile index (N.m/g) in the machine direction of Nomex 410, Nomex 910, Kraft and TUK papers at various initial water contents, impregnated with Nynas Polaris (Pol) or Luminol Tri (Lum)

This array of approaches to comparing paper tensile strengths raises the question of the need for an effective and reliable parameter for monitoring and comparing the mechanical properties of paper at the macro level. In regard to the degree of polymerization (at the molecular level), there is no fixed value that defines end-of-service for cellulose-based paper. However, a DP_v of 200 and lower values have been reported [24-26]. In the case of tensile strength, values of 50% or even 20% of initial tensile strength have been reported as end-of-lifespan indicators [24, 27, 28] .

The cross-direction (XD) tensile index values for Nomex 410 and 910 were analyzed, but the result is not shown in this study. The cross-direction tensile index for Nomex 410 and 910 showed similar behaviour as for machine direction. However, the main difference was the initial tensile index value. In the case of Nomex 410, it was 55 Nm/g. This value is approximately 50% of the machine-direction value. On the other hand, the value for Nomex 910 was 19 Nm/g for an unaged sample. This value is approximately 20% of the initial machine-direction value.

Figure 4 shows the evolution of elongation at break of paper during aging. Nomex 410 (wet and dry) shows a small decrease in elongation during the first 3,000 hours. Between 3,000 and 4,500 hours, this decrease accelerates. After 4,500 hours, Nomex 410 with 2.9% water content (wet Nomex 410) shows a greater decrease in elongation than dry Nomex 410. At the end of aging (7,500 hours), wet Nomex 410 has an elongation of 4.5% while dry Nomex has an elongation of 8.8%. The higher water content in wet Nomex 410 produces a greater decrease in its plastic deformation capacity. This reduction in the elongation capacity of wet Nomex 410 contrasts strongly with the fact that there is almost no change in its tensile index value.

In the case of Nomex 910, its behaviour and values in both cases (in Nynas and Luminol) are similar to those of TUK paper. It is probable that the ductility of the cellulose fibres determines the elongation of Nomex 910. However, the rate of decline in elongation in Nomex 910 was lower (~27% less for the whole ageing duration) than in TUK due to the addition of aramid fibres, even though the high ductility of aramid

fibres was not completely transferred to Nomex 910. This is probably due to the lower quantity of aramid in relation to cellulose in Nomex 910 and because the aramid is found only in the two outer layers of the three layers in Nomex 910. The type of oil used did not show any effect on ductility in Nomex 910.

The cross-direction elongation (not shown here) of Nomex 410 and 910 shows a similar behaviour as for machine-direction elongation. The main difference is the initial elongation value. Nomex 410 has an elongation of 16% (MD) and 10.5% (XD), while Nomex 910 has an elongation of 5% (MD) and 4% (XD). The higher levels with machine direction are probably because the pleat chain structure of aramid is mainly aligned in the MD. As can be observed, a similar effect exists in micro-crepe paper. The addition of nitrogen additives in TUK in combination with aramid fibres (Nomex 910) slows down the rate of reduction in the plastic deformation capacity of the cellulose. Finally, Kraft paper showed the lowest elongation values.

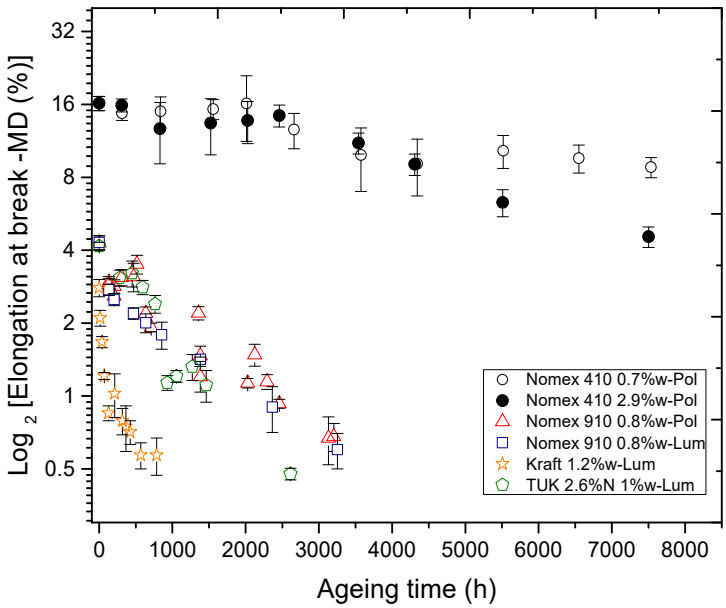

Figure 4: Elongation at break in the machine direction of Nomex 410, Nomex 910, Kraft and TUK papers impregnated with Nynas Polaris (Pol) or Luminol Tri (Lum) at various initial water contents

Based on the trends observed for tensile index and elongation values during aging, it is possible to predict a linear relationship between both parameters for cellulose-based papers (including Nomex 910 – See Figure 5). With the exception of Nomex 410, either elongation or tensile strength can be used to assess the mechanical properties of papers during aging.

On the other hand, the change in ultimate elongation is a more-sensitive parameter for tracking changes in the plastic deformation capacity of Nomex 410. Thus, gradual reduction in the elongation of Nomex 410 and Nomex 910 should be used as a mechanical strength parameter in correlation with a potential aging chemical marker for aramid fibres.

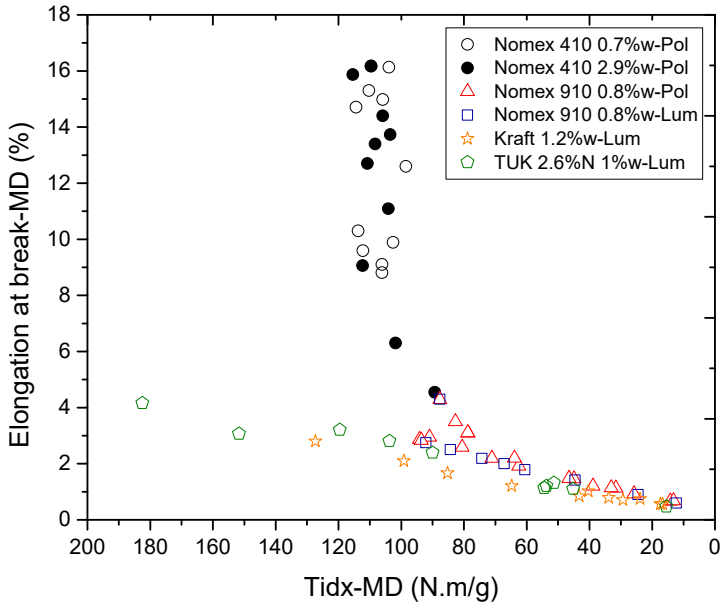

Figure 5: Quasi-linear correlation between tensile index and elongation at break in the machine direction for paper samples

3.2 Change in the degree of polymerization (DP_v) and correlation with tensile index

The change in the degree of polymerization (DP_v) of the cellulose in Kraft and TUK and of the cellulose component in Nomex 910 was measured and compared (see Figure 6).

In all cases, the initial DP_v starts at around 1,200 units. Kraft paper shows the fastest depolymerization of all papers (at 250 hours, the depolymerization of Kraft is 2 and 1.3 times faster than for TUK and Nomex 910). In the case of Nomex 910 (in Nynas and Luminol), the cellulose part depolymerizes more slowly than in Kraft paper due to the nitrogen additives added to the TUK pulp used in Nomex 910. The same conclusion can be drawn for TUK paper. The nitrogen additives slow down the effects of the acid hydrolysis mechanisms on cellulose chains [29]. However, the cellulose in Nomex 910 depolymerizes slightly faster than in TUK paper. This may be due to a higher concentration of nitrogen additives in TUK paper (2.6%N) than in Nomex 910, whose nitrogen additive content is unknown. After the faster cellulose depolymerization in the initial stage and once the nitrogen additives are consumed or transformed, TUK and Nomex 910 papers show a similar depolymerization rate during the last phase of aging. Thus, the aramid fibres in Nomex 910 do not slow cellulose depolymerization by acid hydrolysis.

A large fluctuation in DP_v values was observed for Nomex 910 in Nynas Polaris, unlike the values for Nomex 910 in Luminol. This result is likely due to the steps followed to optimize the DP_v method for Nomex 910. The samples of Nomex 910 in Nynas Polaris oil were used from the start to modify the standard DP_v method. This could explain the outlier data points observed. When the modified DP_v method was improved and optimized, the Nomex 910 in Luminol samples were measured. The change in DP_v of Nomex 910 in Luminol could therefore be considered more representative than those initially measured in Nomex 910 impregnated with Nynas Polaris.

Based on the measurement of the degree of polymerization of the cellulose component of Nomex 910, the mass fraction of aramid fibres was calculated as 33.3% ± 3.06 and 66.7% ± 3.06 for the cellulose. These values were almost constant during aging.

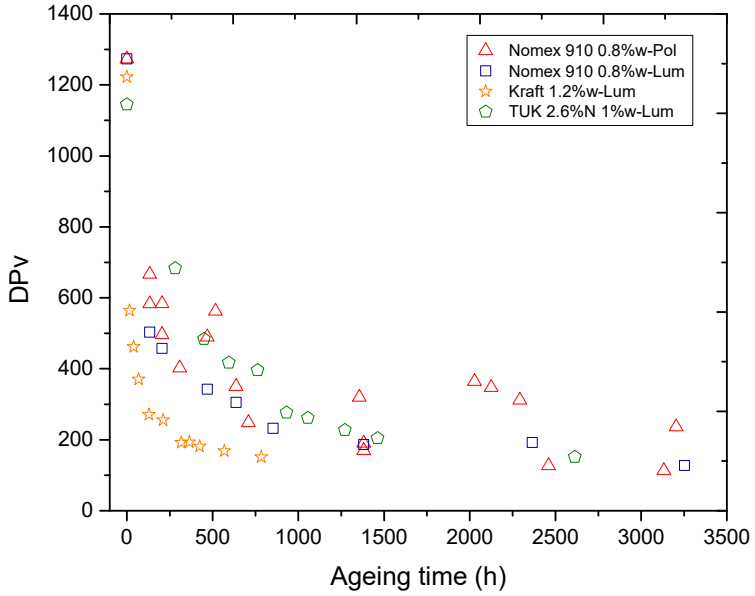

Figure 6: Change in the degree of polymerization (DPv) of Kraft, TUK and Nomex 910 papers during aging

Correlations between the retained tensile index and DP_v of cellulose-based papers are presented in Figure 7. In the case of TUK and Kraft papers, a master curve with two parts was observed.

In the first part of the master curve for Kraft and TUK papers, the retained tensile index is almost constant when DP_v decreases (1,200 to 900 units). This is due to the tensile strength of paper, which is based on the mechanical strength of various hierarchical structures of paper [23] and not only the length of the cellulose chain. In the second part of the master curve, there is a quasi-linear relationship between the DP_v, at the molecular level, and the tensile index, at the macro level. It is therefore possible to affirm that the DP_v and Tidx are intrinsically and physically linked [1, 20]. On the other hand, the Nomex 910 master curve is offset in relation to the TUK/Kraft master curve. This offset is probably due to the mechanical reinforcement of the cellulose matrix with 33% aramid fibre content. This additional enhancement observed for Nomex 910 lasts almost until the cellulose reaches a DP_v of 200 units. After that point, all papers show a similar trend.

Based on the similarities in the master curves for Kraft, TUK and Nomex 910, it is possible to assume that Kraft and TUK aging chemical markers (such as methanol, 2-FAL or furan [1, 3, 22, 30, 31]) could also be used for Nomex 910, probably with the application of an offset factor.

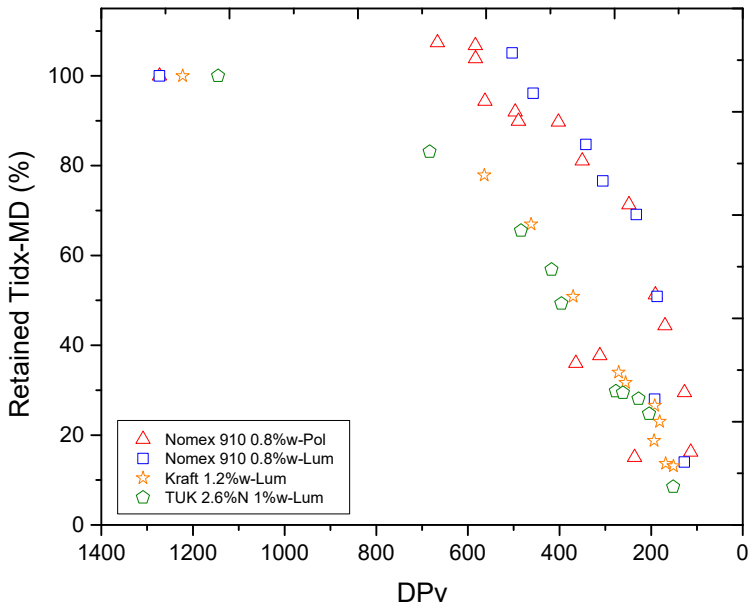

Figure 7: Quasi-linear correlation between retained tensile index (MD) and DP_v

3.3 Fibre morphology and fracture analysis

Figures 8 to 13 provide details on the morphology and fracture characteristics observed in Nomex 410 and 910 during aging.

Figure 8 shows the surface and fracture line of Nomex 910 in Nynas Polaris using a Stemi 2000-CS-stereomicroscope at 5X magnification. Nomex 910 presents dark and irregularly curved cellulose fibres mixed with whitish aramid. It is impossible to distinguish individual aramid fibres or films. The cellulose fibres are aligned to machine direction, but some of the cellulose fibres are randomly oriented. In unaged Nomex 910 paper, the fracture mechanism appears to be driven by the pull-out of cellulose and likely of aramid fibres from the paper matrix. A smaller number of cellulose fibres were broken at the fracture line. Some of the pulled-out cellulose fibres show signs of tearing, which creates fibrils (smaller fibres, see red circle in the figure), but not in the case of aramid fibres. The main fibre pull-out mechanism in Nomex 910 allows for substantial elongation and strength before the sample brakes. Thus, the bonding forces between fibres and in the fibre-matrix should be lower than the fibre fracture force.

After 1,356 hours, the cellulose fibres and surface become darker as result of thermal stress and acid hydrolysis on Nomex 910 components. A mix of fracture mechanisms was observed. A low percentage of cellulose/aramid fibres was pulled out of the matrix, while a high percentage of cellulose fibres broke along the fracture line. At this point, Nomex 910 starts showing brittle fracture behaviour with a dramatic reduction of its plastic deformation capacity, and the matrix-fibre and fibre-fibre debonding forces are higher in certain proportions than the fracture force for aged cellulose fibres. In addition, long pull-out fibres are not observed (see red circle), as they were in unaged paper.

By the end of the aging process, after 3,204 hours, the Nomex 910 fracture type is completely changed. There is almost no evidence of a pull-out of fibres and most of the fibres have broken along the fracture line, maintaining brittle fracture behaviour. The colour of Nomex 910 has become darker, and even some of the cellulose fibres on the surface appears to be black due to thermal degradation. Based on these

results, it is possible to infer that the fracture line goes through the cellulose fibres (the weaker parts), avoiding the aramid fibres, as in the fracture model shown in Figure 2.

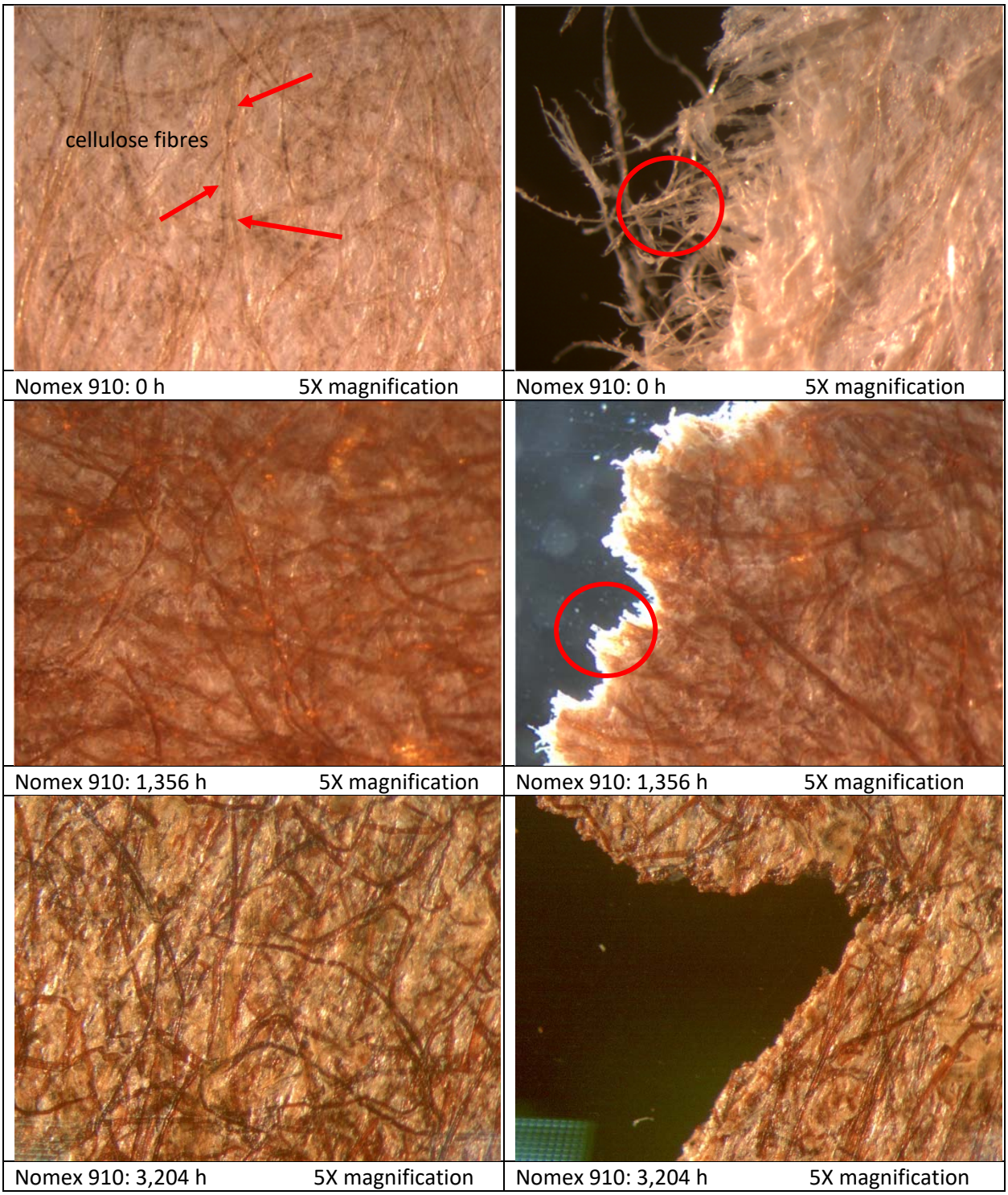

Figure 8: Microscope images of the surface and fracture line of Nomex 910 in Nynas Polaris at 170°C with initial 0.8% water content at various aging times

Figure 9 shows the surface and fracture line of Nomex 410 with initial 0.7% water content in Nynas Polaris using a Stemi 2000-CS-stereomicroscope. Straight whitish aramid fibres are aligned in the machine direction. However, a small number of the fibres are randomly oriented. In addition, individual aramid films cannot be distinguished on the surface. From the beginning to the end of aging, fibre pull-out with no presence of fibrils (see red circle) is the main fracture mechanism for Nomex 410.

At 3,574 hours, Nomex 410 exhibits ductile fracture behaviour. This allows for greater material deformation before Nomex 410 breaks. Small pieces (see red circles) along the fracture line were observed and appear to be agglomerates of aramid pulled from the matrix. It is not clear if these aramid sections are detached or broken. The presence of long, pulled-out fibres confirms the significant elongation observed at this point.

At the end of the aging process, after 7,534 hours, the fracture behaviour of Nomex 410 changes. The length of the pulled-out fibres becomes shorter (see red circles) in comparison with unaged paper. This change is probably the result of the impact of hydrolysis on the plastic deformation capacity (elongation) of Nomex 410. In addition, a paper colour change from whitish to grey with dark spots was also observed. The paper colour variation could be related to the rupture and rebuilding of hydrogen bonds between aramid fibres during the hydrolysis reaction [32].

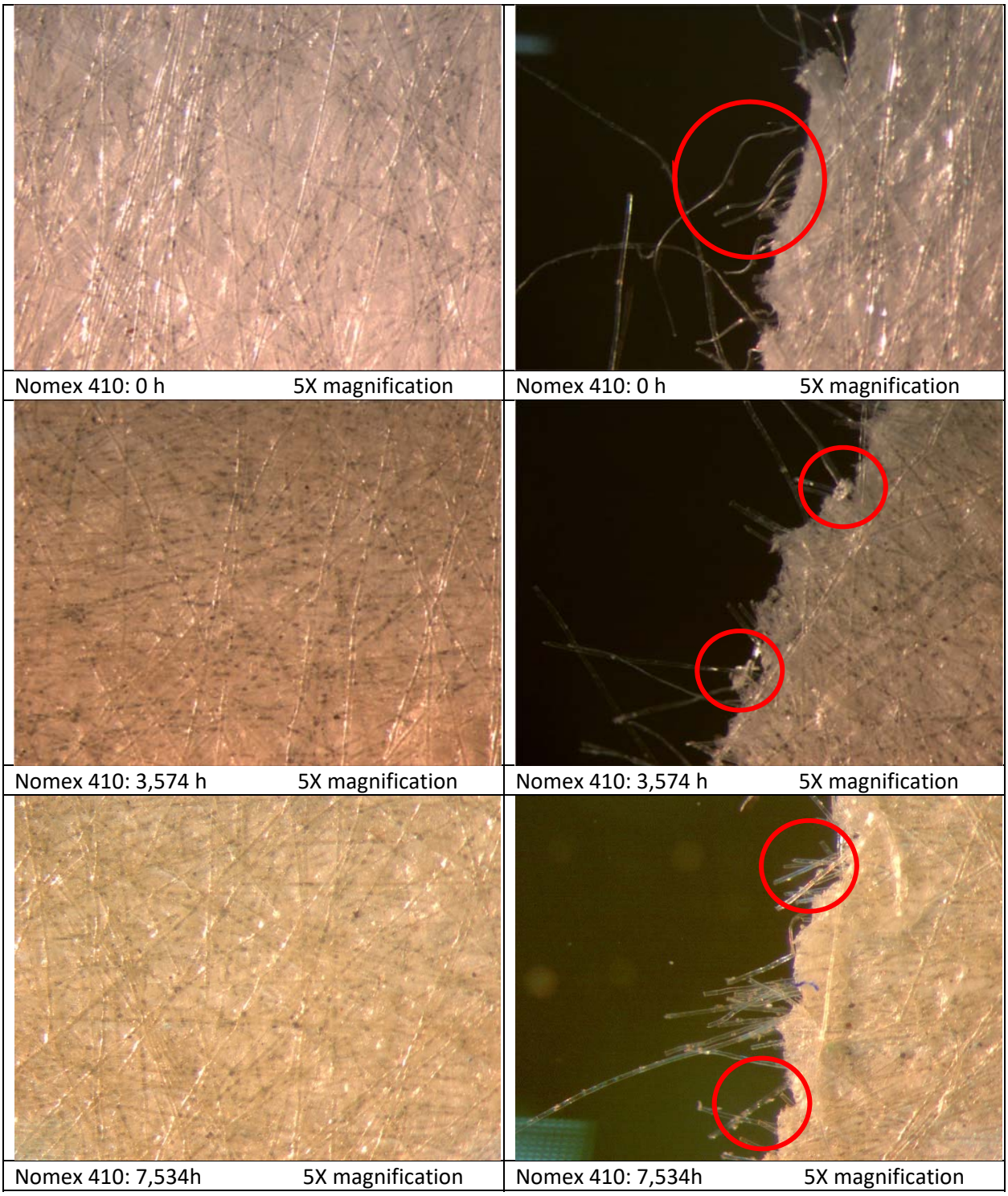

Figure 9: Microscope images of Nomex 410 surface and fracture line with initial 0.7% water content in Nynas Polaris at 170°C at various aging times

Figure 10 shows a Nomex 910 surface at higher magnification than in Figure 8, using a Nicolet iN10-infrared microscope.

With the exception of the colour change and the presence of dark spots, the morphology of the Nomex 910 surface remains almost unchanged during aging. The irregularly shaped cellulose fibres are oriented mainly in the machine direction along the paper surface. The thickness or diameter of the cellulose fibres is not uniform, and fibre dispersion is also non-uniform. The cellulose fibres become darker as aging advances.

The aramid (fibre/film forms) appears to be entangled and somewhat hidden among the cellulose fibres. However, it is possible to differentiate the aramid fibres because they have symmetrical tubular shapes and their average diameter is smaller than that of the cellulose fibres. The brownish colour observed for aramid fibres is possibly due to a light effect or because part of the cellulose covers the aramid fibres. It was not possible to distinguish individual film-form aramid. However, the aramid component could be differentiated from the cellulose by the whitish areas surrounding the cellulose fibres. As aging progresses, more dark spots along the surface of Nomex 910 were observed. The origin of these dark spots is unknown, but their presence could be related to the effect of hydrolysis on the aramid component.

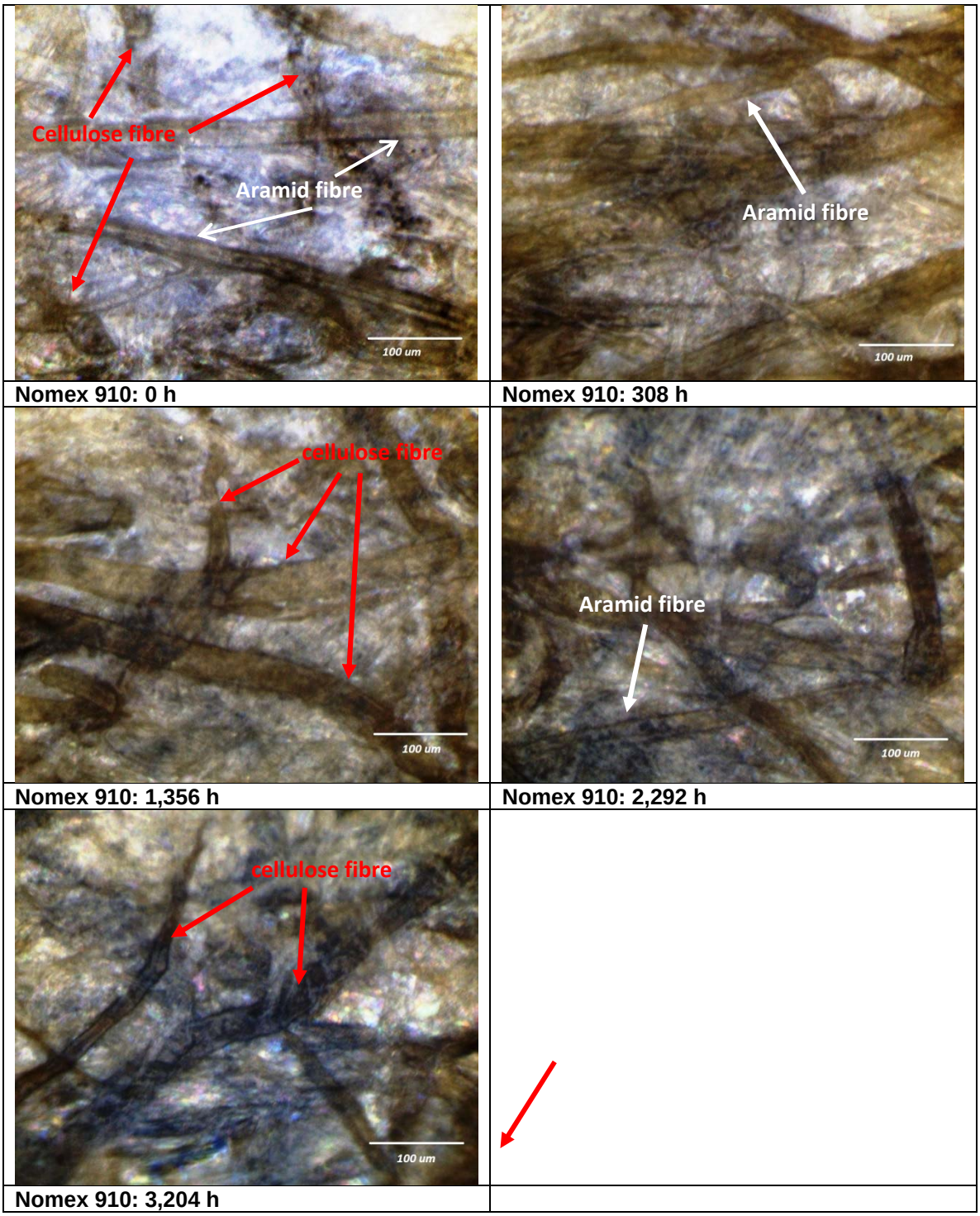

Figure 10: Microscope images of the surface of Nomex 910 with initial 0.8% water content in Nynas Polaris at 170°C at various aging times

Figure 11 shows the surface of Nomex 410 using a Nicolet iN10-infrared microscope. There was almost no change in the surface morphology of Nomex 410. This was similar to that observed in Nomex 910, with the exception of the marked presence of black spots observed at the end of aging. The Nomex 410 surface is composed of aramid fibres and aramid films in similar percentages. The long straight aramid fibres are aligned in the machine direction and they do not fold or bend like cellulose fibres. However, they have a non-uniform dispersion. The microstructure of the aramid fibres is very stable with no change in diameter or shape during aging. In the case of aramid films, no individual films can be observed, either because an aramid film covers the observation area or the films agglomerate and the edges become blurred. Black spots (see circles) were noticed in Nomex 410, even in unaged conditions. At the end of aging, a greater number of randomly located dark spots was observed. The origin and apparently random location of these spots are unexplained. However, the significant presence of dark spots at the end of aging could also be related to the adhesion of oil degradation products over the surface of the Nomex 410 or the effect of hydrolysis on aramid.

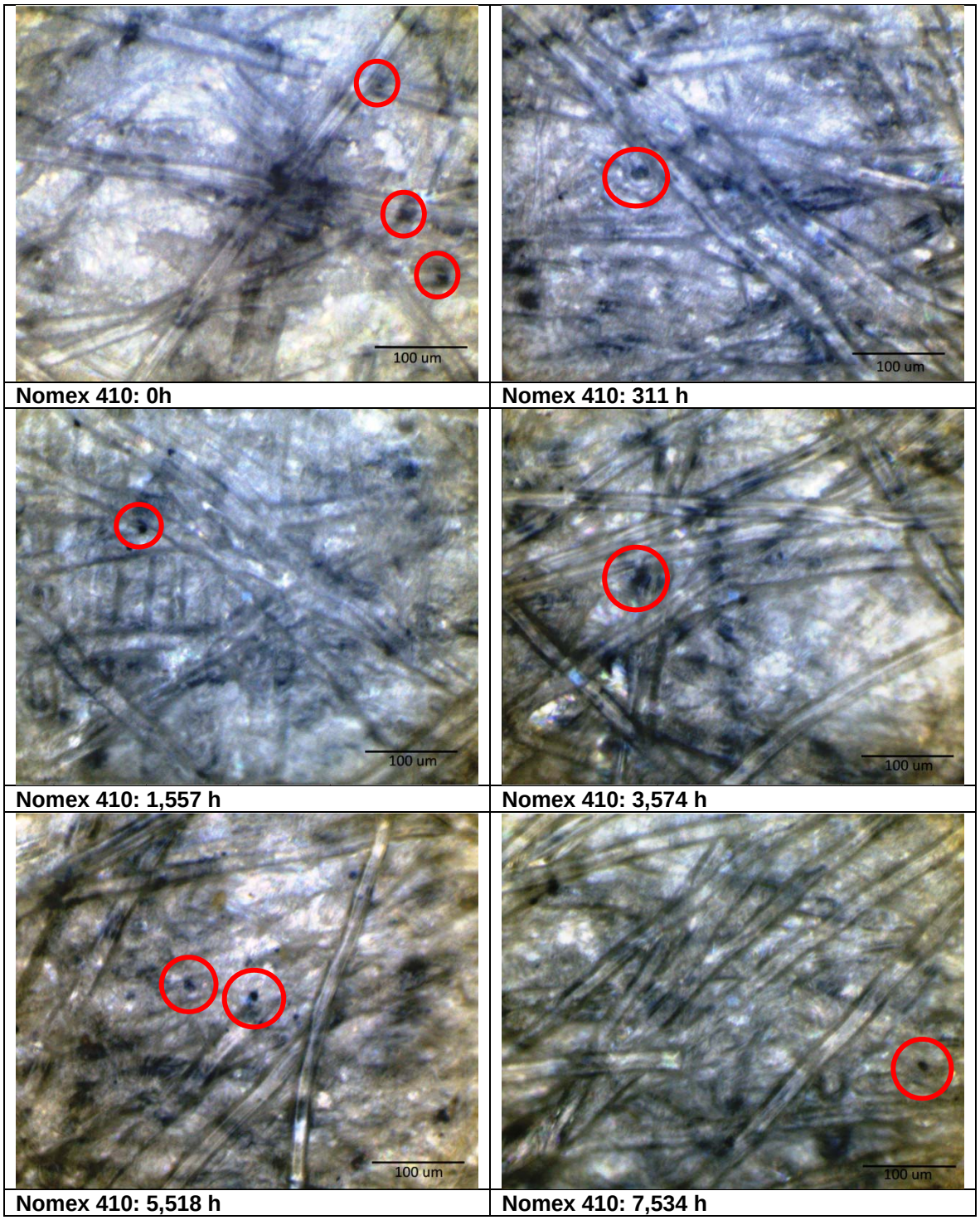

Figure 11: Microscope images of the surface of Nomex 410 with initial 0.7% water content in Nynas Polaris at 170°C at various aging times

Figure 12 shows SEM images at 450 and 2,000 times magnification of the Nomex 910 with initial 0.8% water content at various aging times.

In unaged conditions, the cellulose fibres and aramid fibre/film are not well defined on the paper surface. However, the aramid fibres are slightly easier to identify due to their regular shape and thickness, and the irregularly shaped fibres are therefore cellulose. The film-shaped aramid (fibrids) covered or wrapped the cellulose and aramid fibres.

At 1,356 hours, a rough surface gradually appears with the presence of cracks and depressions or cavities (see circles). In addition, noticeable spaces along the length of the fibres are observed. This could be a sign that the bonding forces between the fibres and matrix are weaker. At this point, the cellulose component of Nomex 910 has a DP_v of 320, which probably indicates that the aramid component determines the mechanical strength of Nomex 910.

At the end of the aging process, at 3,204 hours, a very coarse surface of the Nomex 910 is visible. There are more surface cracks, and they are bigger (see circles). This should lead to a greater reduction of fibre-fibre and fibre-matrix bonding strengths. At this point, the Nomex 910 is a very fragile and brittle material.

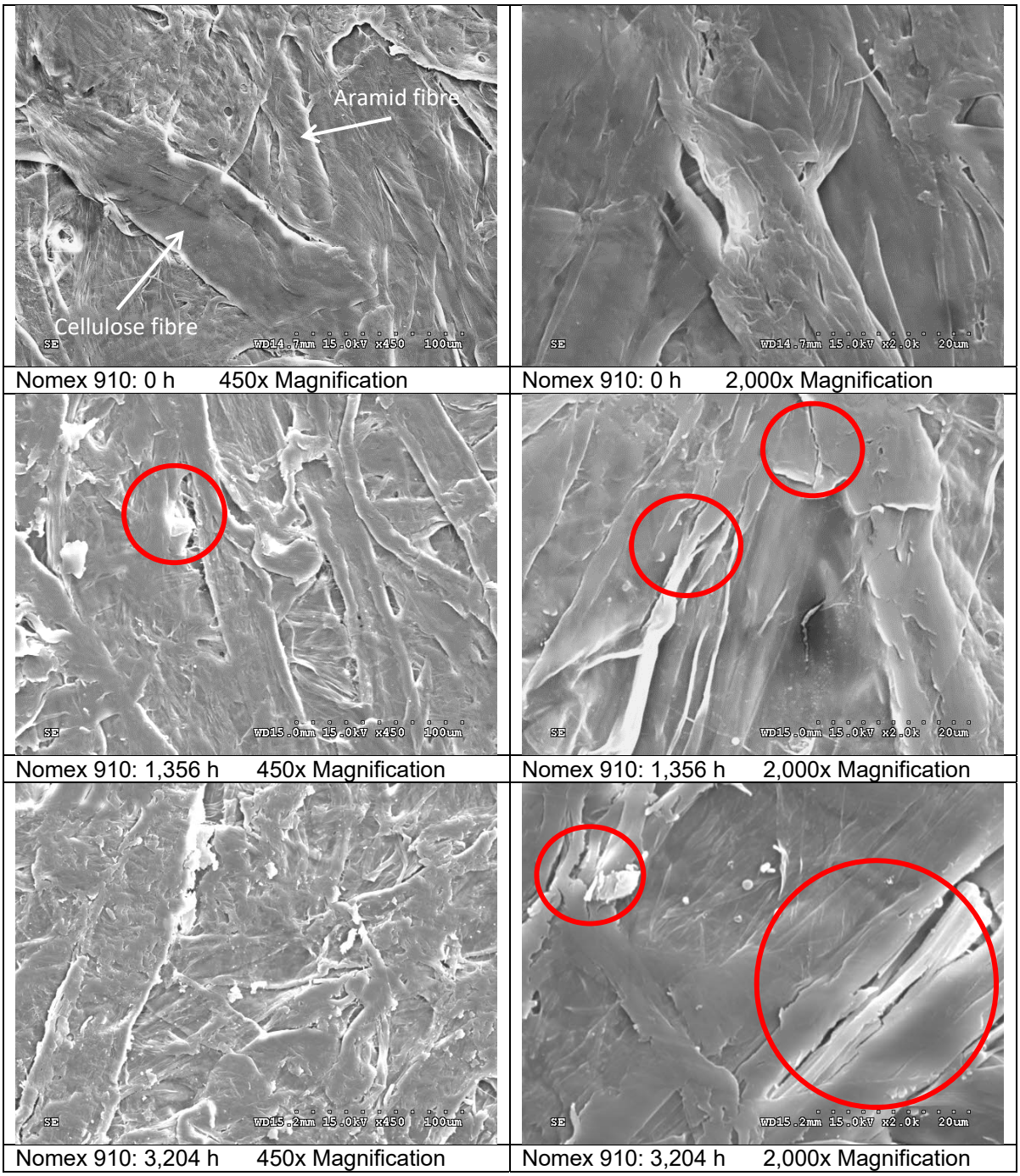

Figure 12: SEM images of the surface of Nomex 910 with initial 0.8% water content in Nynas Polaris at 170°C at various aging times

Figure 13 shows SEM images at 450 and 2,000 times magnification of Nomex 410 with initial 0.7% water content at various aging times. The Nomex 410 surface does not present any major changes during accelerated aging. The only noticeable aspect is the lack of uniformity and low dispersion of the aramid fibres (e.g., different orientations and two or three fibres are very close, see red circle at 5518 hours).

In unaged condition, the Nomex 410 surface shows the presence of straight fibres of aramid (flocs) enveloped by aramid films (fibrids). It appears that the aramid films are also intercalated, forming a wall structure or sandwich with the aramid fibres in the middle.

At 5,518 hours, the surface of Nomex 410 did not present any noticeable change compared to the new material.

At the end of aging, at 7,534 hours, the Nomex 410 surface shows the presence of depressions (see circle), but no fractures or cracks, as well as some holes in the aramid film. However, the holes could have been created by the SEM beam.

It is not possible to relate the decrease in elongation to the subtle changes detected in the aged microstructure of the Nomex 410. However, the surface of the aramid fibres appears to be rough when compared to the unaged fibre.

The presence of white particles (see triangles) was detected on the surface of the Nomex 410 samples during aging. The energy-dispersive X-ray spectroscopy (EDS) analysis shows that these particles are rich in bismuth (Bi). The particles appear to maintain the same size during aging. The bismuth has high electrical resistivity. The possibility that the bismuth was an additive in the mineral oil was discarded. The origin or source of the bismuth is unknown.

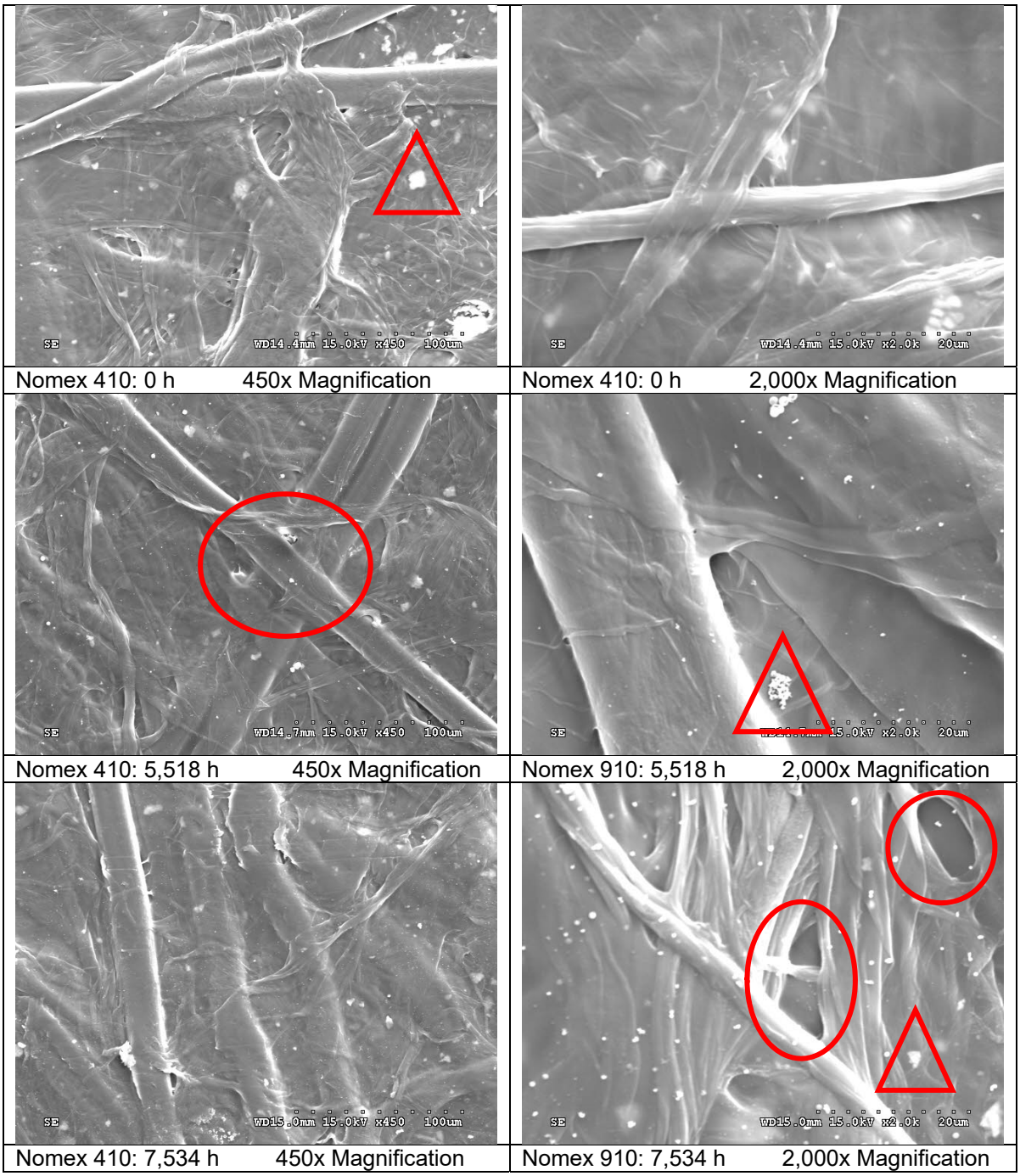

Figure 13: SEM images of the surface of Nomex 410 with initial 0.7% water content in Nynas Polaris at 170°C at various aging times

4. Conclusions

This study presents changes in the mechanical properties of papers based on aramid (Nomex 410) and cellulose (Kraft, TUK and Nomex 910) impregnated with insulation fluids (Nynas Polaris and Luminol Tri) at thermally accelerated conditions (170°C).

Nomex 410 with 0.7% water content exhibits very stable tensile strength performance during aging (around 7,500 hours). However, Nomex 410 with 2.9% water content shows a large decrease (around 20%) in tensile strength at the end of aging. Plastic deformation capacity (elongation) during aging was also reduced in Nomex 410 at both water content levels. However, the largest loss was observed in Nomex with 2.9% initial water content. These changes in the mechanical properties of Nomex 410 are related to the combined effect of high temperature and the hydrolysis mechanism on the aramid fibres.

Nomex 910 is an aramid-enhanced cellulosic paper. It is composed of a central layer of cellulose reinforced with lateral layers of aramid/cellulose fibres. Nomex 910 shows superior behaviour in terms of the retained percentage of tensile index when compared to TUK paper. However, TUK paper shows higher or similar tensile strength values compared to Nomex 910, with the exception of the last aging phase, when Nomex 910 exceeds TUK performance due to the addition of aramid fibres.

It was assumed that the fracture's inception in Nomex 910 should be found in the weakest area. The weakest zone of Nomex 910 is likely the central cellulose layer.

Measurement of the DP_v of the cellulose inside the Nomex 910 was performed using a variant of the method used for Kraft and TUK paper.

A quasi-linear or master curve between DP_v and tensile strength was observed for the cellulose-based paper, including Nomex 910. However, the linear correlation was offset for Nomex 910 due to the addition of aramid fibres in its matrix. It is also likely that the same chemical markers used to track the aging of Kraft and TUK papers could be adapted and applied to Nomex 910.

The reduction in elongation over time and, to a lesser extent, in the tensile strength of Nomex 410 and 910 could be used as a monitoring tool to potentially determine the state of solid insulation in power transformers containing meta-aramid papers as the main solid insulation system.

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