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The key learning's of developing the Bloom technology

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- Italian, living in The Netherlands
- University of Eastern Piedmont “Amedeo Avogadro”
- Background in Analytical and Polymers Chemistry
- 7 years working experience in the field of High Pressure Laminates (HPL) production
- Area of expertise: thermosetting resins, paper impregnation, pressing wood composites, natural biobased polymers (e.g. lignin).

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Agenda

1. Nemho and Broadview Materials companies
2. High Pressure Laminates (HPL)
3. Bloom technology
4. Key learning of LPF resin development
5. Lignin requirements
6. Lignin activation by methylolation
7. Conclusions
8. Questions

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Nemho and Broadview Materials companies

Broadview holding is an international holding that is currently active in two industry clusters:

- Energy
- Material Technology

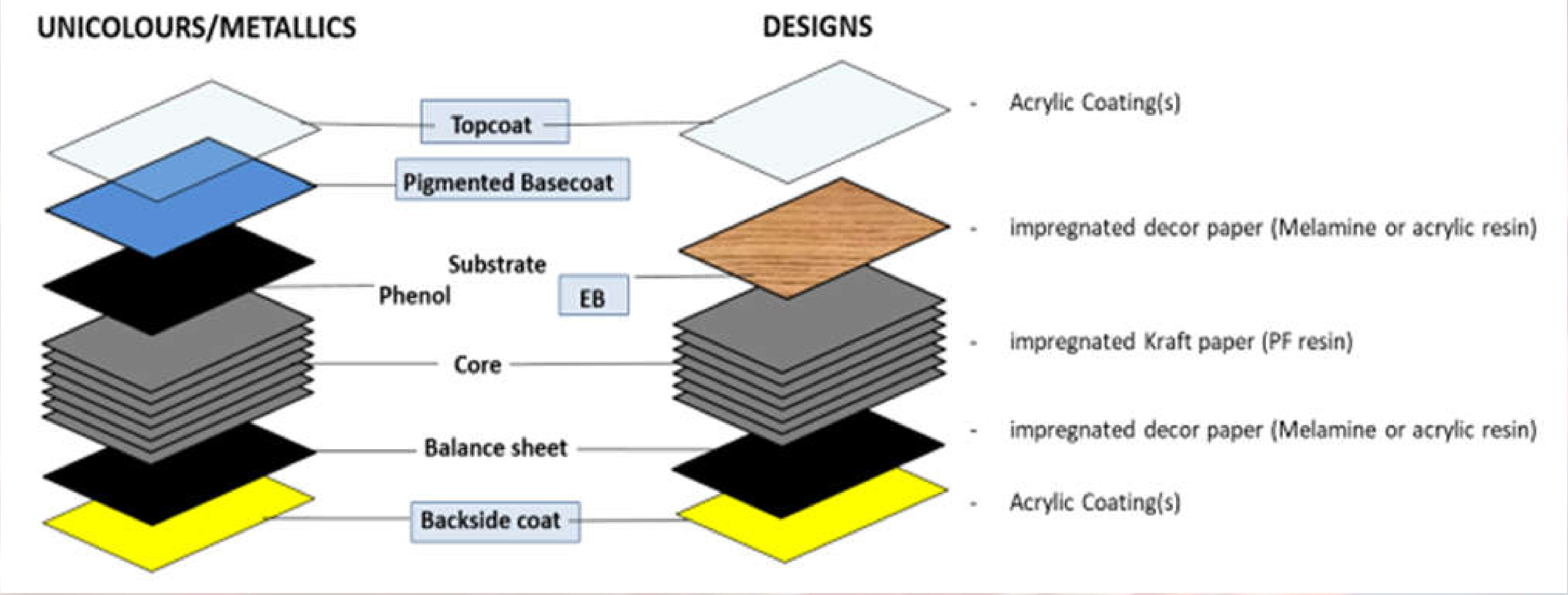
In the Material Technology branch of the holding, Broadview is owner of several companies:

- Trespa International B.V.
- Arpa Industriale S.p.A.
- Westag & Getalit AG (owned 62.3%)
- Homapal
- Formica group consisting of Formica EMEA, Formica Asia and Formica NA

These manufacturing companies are supported by Nemho – the Next Material House – as the center of excellence for technology in the group. The research and development for all the different companies is performed by the Nemho R&D group.

High Pressure Laminates (HPL)

- Laminates are products that are made of multiple layers of semi-finished material (in general impregnated papers), that are then compressed and fused together.
- In general, laminate products typically contain about 70 wt% wood derived material (e.g. fibers or paper) and about 30 wt% thermosetting resin.
- The fusing of the compressed stack of layered semi-finished material is accomplished by the polymerization reaction of the thermosetting resin; which is normally driven by the application of heat and taken to a desired degree of final curing.



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Bloom technology: beyond the surface

Sustainability is not something you dream about, but something you do. It's about acting. True to this vision, Arpa Industriale and Nemho have developed Bloom, a new core technology for FENIX NTM® and Arpa HPL.

Arpa HPL products are made of paper and thermosetting resins based on phenol. With Bloom, lignin technology has been introduced to significantly reduce the amount of phenol included in the resin by 50%. Lignin is a natural polymer defined as the glue that holds wood fibers together.

Technology is nothing without a good storyline

Key learning's of developing the Bloom technology

In 2012 the Nemho R&D group started the "Lignin Project" to substitute partially the phenol with lignin (50% achieved in Bloom technology) in order to:

- Improve sustainability of resins and related products (LCA)
- Reduction of formaldehyde emissions of semi-finished material
- Have more stable cost of raw materials, phenol price fluctuate based on oil price
- Phenol is toxic / harmful raw material

In the Bloom technology kraft paper is impregnated with Lignin - Phenol - Formaldehyde (LPF) resin instead of standard Phenol - Formaldehyde (PF) resin.

LPF impregnated kraft sheets are assembled with décor sheets and then pressed in a multidaylight pressing process.

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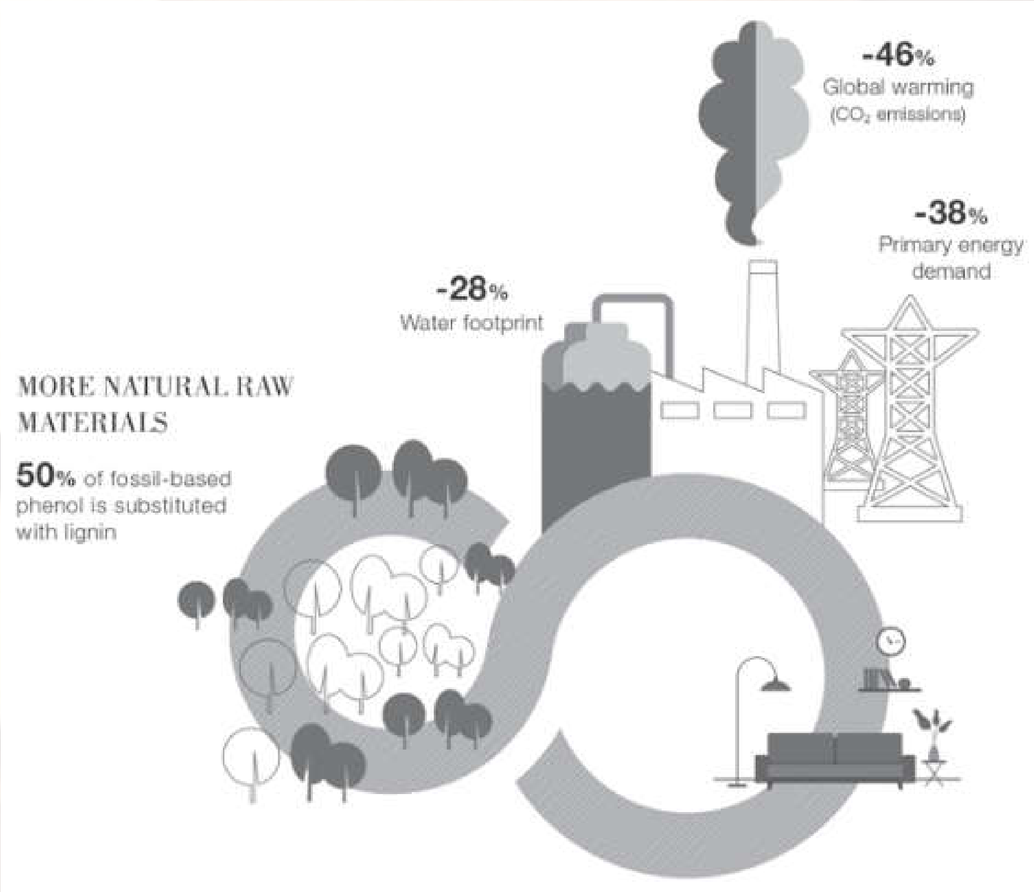
Life Cycle Assessment (LCA)

At Nemho we measure sustainability by Life Cycle Assessment in order to evaluate the environmental impact of a product through its life cycle (e.g. extraction and processing of the raw materials, manufacturing).

With Bloom technology we have been able to:

- Cut greenhouse gas emissions by 46% (Global Warming)
- Decrease primary energy demand (amount of energy extracted from the natural environment) by 38%
- Decrease water footprint by 28%



*** Source:** *LCA study performed by Arpa Industriale comparing standard FENIX NTM and Arpa HPL with new FENIX NTM Bloom and Arpa HPL Bloom.*

Main characteristics of LPF resins for HPL production

- Viscosity should be at same level than the currently available PF resins.
- Free-formaldehyde in resin, impregnated kraft and final laminate product should meet current regulations.
- LPF resin should be enough stable (shelf-life) to enable storage and processability after resin production (stable viscosity for a period of 2 weeks).
- Resin reactivity should be adaptable to industrial process (impregnation and pressing).
- Solid content should not be significantly lower than PF resin in order to avoid additional costs related to cost of transportation and also additional costs during paper impregnation process (more water => less resin => lower paper converting speed due to additional needed energy => higher costs).
- Quality of final resin should be enough stable not to cause process variations.

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Key learning's of developing the Bloom technology

Quality of final HPL laminate products are strongly influenced by quality of lignin used in the LPF resin:

- Lignin source (e.g. lignosulfonates, kraft, organosolv)
- Lignin Mw
- Ash and carbohydrates content
- Lignin functional groups
- Solubility

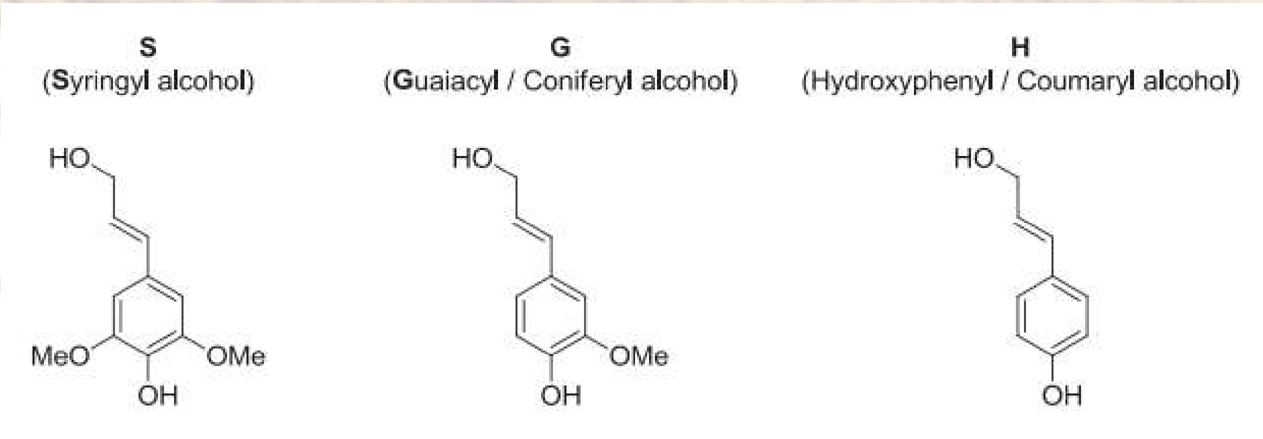
Property	Lignosulfonates	Kraft lignin	Organosolv. lignin
Molecular weight (g/mol)	20,000 – 50,000	2,000 – 5,000 *	< 3,000
Polydispersity	6 - 8	2 - 4	2.4 - 6.4
Residual carbohydrates (%)	10 - 25	1 - 3	0,3 - 1
Sulfonate (mg/g)	1.25 – 2.5	0	0
Organic sulfur (%)	4 - 8	1 – 1.5	0
Color	Brown	Brown	Brown
Solubility	Soluble in H_2O Insoluble in organics	Soluble in alkali (pH>9.5)	Insoluble in water Soluble in alkali and many organic solvents

** Typical LignoBoost lignin Mw is in range of 3000 – 4000 g/mol*

Key learning's of developing the Bloom technology

Complications:

- Active sites on the aromatic ring of lignin are rare or sterically hindered
- High Molecular weight (Mw)
- Methoxy groups limit the reactivity on the aromatic ring
- Slower reaction than phenol
- Lignin characteristics are different per type of wood and production process



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Lignin requirements

- Lignin source:
  - ✓ Performance of lignin powder is a combination of:
    1. Lignocellulosic material used as feedstock in the fractionation process (e.g. hardwood, softwood, grass).
    2. Accessibility and number of lignin functional groups (e.g. phenolic –OH) and reactive sites on the aromatic ring.
    3. Mw of lignin.
  - ✓ The fractionation process of the lignocellulosic material is influencing the final properties of lignin. Each lignin grade needs to be tested separately whether it would be suitable for the LPF resin.
- Lignin Molecular Weight (Mw):
  - ✓ Mw of lignin is impacting viscosity of final resin and thus LPF performance during impregnation process.

Lignin requirements

- Ash and carbohydrates content:
  - ✓ Amount of ashes and carbohydrates influence final laminate properties. They make final wood product absorbing more water (any type of salts likes to absorb water).

- Lignin functional groups:
  - ✓ Phenolic –OH: this groups influence in a positive way the reaction between lignin reactive sites and formaldehyde and further cross-linking.
  - ✓ Carboxylic acid: this groups influence in a positive way solubility of lignin into water but negatively properties of final wood product.
  - ✓ Catechol: this groups influence in a positive way the reaction between lignin reactive sites and formaldehyde and further cross-linking. Based on our experience the amount of catechol groups should be as high as possible in order to enhance the reactivity of lignin.

The ideal lignin has lower Mw, it is easy to dissolve in water at pH 9,0 and it has high amount of phenolic –OH and catechol groups.

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How we characterize the lignin at Nemho

- Measure lignin dry content, pH and ash content
- Determine lignin Mw by Size Exclusion Chromatography (SEC)
- Determine amount of functional groups by 31P NMR
- Solubility test: dissolve powder lignin into water/alkali solution at pH > 9,5
- Reactivity test:
  1. Dissolve powder lignin into water/alkali at pH = 9.5
  2. Mixing for 2 h at 70°C
  3. Addition of xxx moles of Formaldehyde / grams of Lignin
  4. Reaction for 1h at 70°C
  5. Measure formaldehyde conversion (amount of reacted formaldehyde per dosed formaldehyde)

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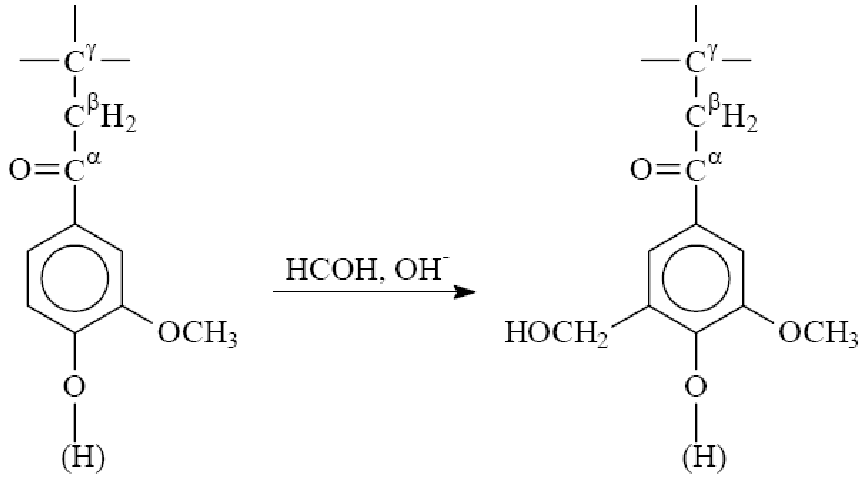
Lignin “activation” by methylolation (Trespa patent WO2018190720)

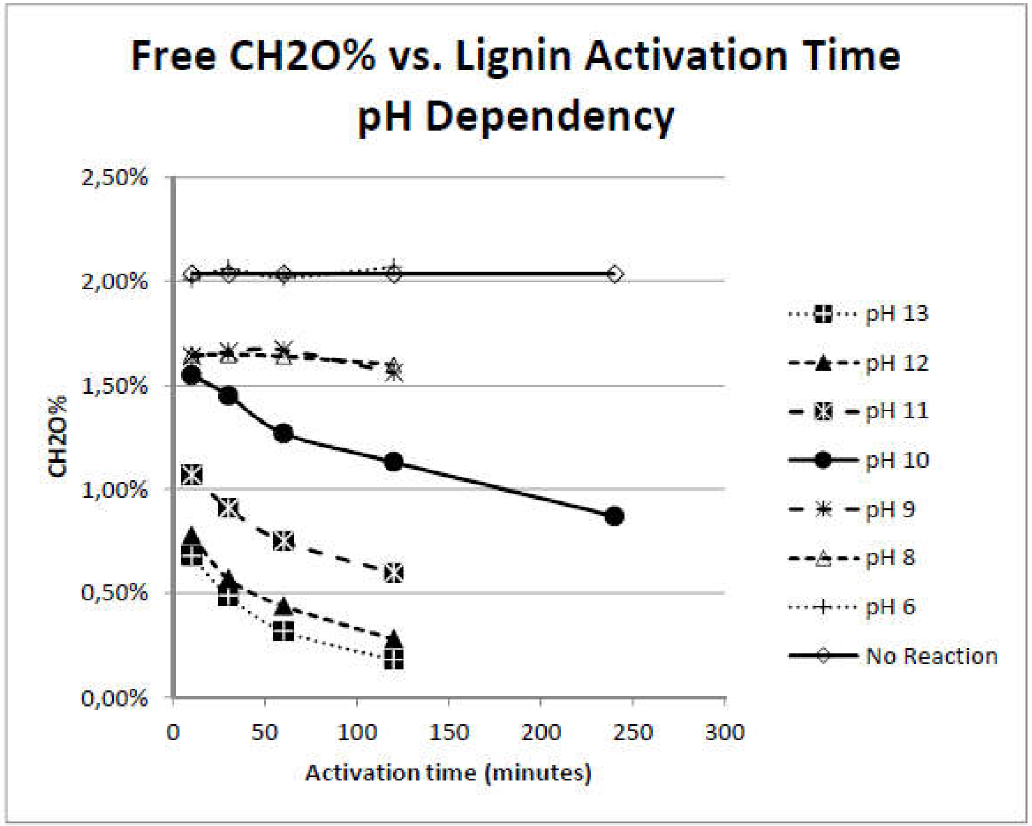
In order to improve cross-linking of lignin with phenol, the lignin is “activated” before resin synthesis utilizing formaldehyde.

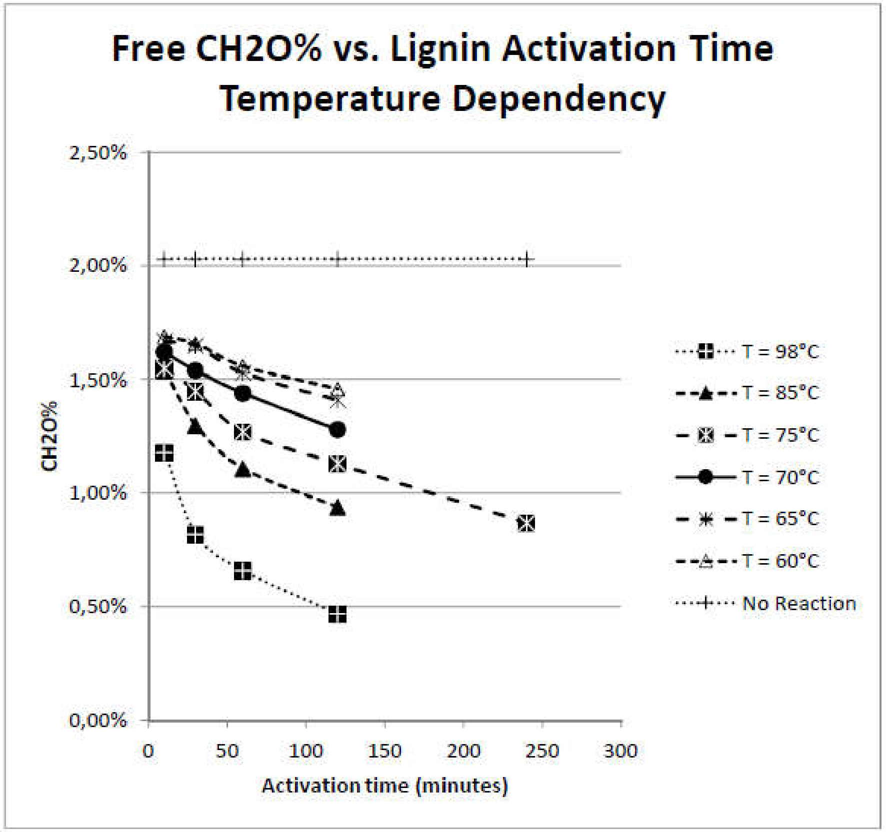
Main process parameters influencing reaction between lignin and formaldehyde are:

- Lignin functional groups
- Active sites on aromatic ring
- pH
- Reaction temperature
- Reaction time



Lignin “activation” by methylolation (Trespa patent WO2018190720)





- Formaldehyde concentration decreases with the hold time of the activation step, and the rate of this decrease is related to how alkaline the batch is.

- Formaldehyde concentration decreases with the hold time of the activation step, and the rate of this decrease is related to how high the temperature is (pH was kept constant).

Lignin "activation" by methylolation (Trespa patent WO2018190720)

- In order to determine if formaldehyde actually reacted with lignin reactive sites, 2D NMR is normally performed.

		Liquid Lignin	60min. activation	120min. activation
Example 4 (Kraft)	Methylol (-CH_2OH) signal	No signal	Strong signal	Slightly stronger signal
	Guaiacyl unit G5 active hydrogen signal	Strong signal	Weak signal	Slightly weaker signal
Example 16 (Na Lignosulphonate)	Methylol (-CH_2OH) signal	No signal	Strong signal	Slightly stronger signal
	Guaiacyl unit G5 active hydrogen signal	Strong signal	Weak signal	Slightly weaker signal

- The lignin methylol signal seen in the 2D NMR is proportional to the amount of formaldehyde consumed in the lignin activation step.

- The lignin methylol signal is inversely proportional to the G5, H3 & H5 signal region, which suggests that methylolation is taking place predominantly at these positions.

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Conclusions

- Bloom technology has been introduced at Arpa to reduce by 50 % the amount of phenol included in the thermosetting resin. This has resulted in a greater environmental performance of e.g. -46 % CO_2 emissions.

- Main LPF resin attributes to be considered during resin development are viscosity, solid content, free-formaldehyde, reactivity (measure using rheometer) and shelf-life of final resin.

- Main lignin requirements for development of LPF resins are related to type of feedstock used during production process, type and amount of functional groups (e.g. phenolic –OH), availability of reaction sites on aromatic ring, Mw, ash and carbohydrates content.

- One way to activate lignin before resin synthesis is by methylolation with formaldehyde in order to improve cross-linking of lignin with phenol (Trespa patent WO2018190720).

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ANY QUESTIONS?

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