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Section 4 **Processes and properties**

Organosilicon-based impregnation hydrophobers for wood

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ABSTRACT

The SILEX project “Improving sustainability of construction materials using innovative Silicon based treatment” is a Life+ project with reference LIFE+11 ENV/BE/1046 and started in April 2013. This project intends to demonstrate that a new class of compounds can be used for wood treatment for an extended service life combined with enhanced new testing methodology. The project aims at demonstrating that treatments with silicon-based hydrophobers opens the door to minimize the use of biocides.
This paper gives some results related to the impact of silicon-based water repellent on water absorption, moisture dynamics and biological resistance of treated wood.

Keywords: organosilicon compounds, hydorphobation, moisture dynamics

1. INTRODUCTION

Wood is an important renewable construction material. Beside its use indoor (for furniture or wood house structure), it is also frequently used for outdoor application, whether for furniture, decking or cladding. Wood is subject to water infiltration by both liquid and vapour. As the moisture content increases, the wood will swell until it reaches its maximum dimension at its fibre- saturation point. Rapid dimensional changes resulting from changes in the level of bound water cause the wood to crack and split. These cracks will then allow moisture to absorb easily and quickly into the wood. At some moisture content levels and depending on the time of wetness moisture will be present as free water, which in turn promotes the rate of wood decay.
Both physical and biological degradation are greatly reduced when water penetration is dramatically reduced (by coating or impregnation) and/or when wood is modified (by chemical or thermal treatment). This paper is concentrating on potential methods to minimize liquid water penetration of treated wood when non film forming hydrophobers are used. Silicon-based hydrophobers have demonstrated their benefit to reduce water penetration in many inorganic construction materials (ranging from clay based – bricks to cement based – concrete-mortar) (Howells 2009). Several studies explored their use as hydrophober for wood as well (De Vetter et al. 2009, 2010, Mai and Militz, 2004, Ghosh *et al.* 2009, 2012).

This study is part of the so-called SILEX project “Improving sustainability of construction materials using innovative Silicon based treatment” which is a Life+ project initiated in 2013.
This project intends to demonstrate that organosilicon compounds can be used for wood treatment for extended durability and that the testing phase could be accelerated according to new testing methodology.

This update of the project intends to present some results showing potential to use this technology.

2. MATERIALS AND METHODS

2.1 Siloxane and alkoxy silanes

Silicone is a generic term describing polymers based on a siloxane backbone (based on the repeating unit: Si-O-Si). **Polydimethylsiloxanes** or PDMS (Figure 1) are the most common siloxanes used worldwide. Polydimethylsiloxanes are available as low or high viscosity fluids. Terminated by a silanol group (Figure 1), they are reactive. Their low surface tension, better resistance to UV radiation vs. organic polymers and high gas permeability are of great benefit in the field of hydrophobic treatment.

Silanes are molecules based on one silicon atom which bears four substituents. Alkyl trialkoxy silanes (Figure 1) are used in hydrophobic additives, either for post-treatment or admixture as they have good reactivity towards inorganic, silanol-rich surfaces. The aliphatic chain (i.e. isobutyl or octyl chain) confers the hydrophobic character to the treated substrate. Upon hydrolysis and condensation, silanes create a resinous network which bonds covalently to the surface of treated materials leading improving water resistance durability.

Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of individual or mixtures of silanes (Figure 1).
Silicone resin with silanol or alkoxy groups and hydrophobic alkyl groups can be designed such as to diffuse within a matrix and react with reactive groups. The reaction can lead to a chemical anchorage to the treated materials.

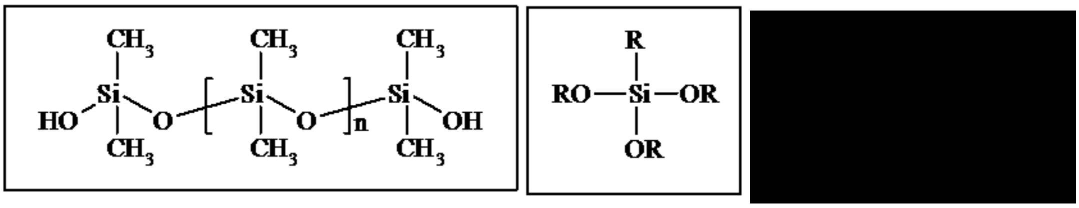

Figure 1 : structure of polydimethylsiloxane, alkyl trialkoxysilane and schematic representation of a silicone resin (R can be ethoxy, methoxy, R1 can be methyl, phenyl or octyl group)

It is often the case that the chemicals used as water repellents need to be further formulated to enable their effective use. This additional formulation step will be named here as the delivery system. For example, water repellents can be used as such, diluted in solvent, or emulsified. The delivery system needs to be adapted to the application method. Water repellent based formulated with different delivery systems were used in this study. A water soluble silane was used, which simply require to be diluted in water. Two oil in water emulsions were used. Water soluble silane or oil in water emulsion can be used for simple post-treatment or vacuum impregnation. An oil based formulation was used in this study, but obviously applied only by brushing/wiping.

2.2 Wood specimens and test protocols

Scots pine and beech samples ((50 ± 0.5) mm * (25 ± 0.5) mm * (15 ± 0.5) mm) without visible defects were selected.

Silicon-based water repellents were supplied by Dow Corning. A water soluble silane functionalized with an amine (SIL A) was used to assess performance of water repellent which could go as deep into wood structure as water. A non ionic emulsion of a mix of polydimethylsiloxane, silane and silicone resin was used (EM A). This mix of active component is typical for a "general purpose" water repellent for inorganic construction material. A cationic emulsion of an organofunctional siloxane (EMU B) as well as a microencapsulated siloxane polymer (MIC A) were used. A mix of a silicone resin and silane was tested (RES A) (applied only by brushing)

Laboratory vacuum impregnations were carried out on Scots pine sapwood, beech and oak specimens. Wood specimens were dried in an oven at 60°C till constant weight. They were then introduced in a glass flask put under vacuum once closed. Wood samples were submitted to a vacuum of 50 mbar for 20 minutes. 1500 g of diluted silicon-based water repellents were added under vacuum. Dilution were adapted such as to contain 1 % of active material. Air was then released into the vacuum vessel till atmospheric pressure. Samples were kept in the glass flask full of solutions for 20 minutes. Samples were finally left in the lab to allow drying and further dried in an oven at 60°C till constant weight. Samples were weighed before and after treatment to calculate the Weight Percent Gain (WPG) calculated as follow in Eqn.1 with Wi as the initial weight and Wf as the weight of the sample impregnated after drying at 60°C till constant weight.

$$WPG = (Wf - Wi)/Wi \qquad (1)$$

Water uptake was calculated to study the absorption and desorption rate of the treated wood. Samples were put in contact with water to measure "longitudinal" water absorption. Wood specimens were removed, blotted and weighed at regular time intervals.
The drying rate was assessed by removing wood specimens from water after 72 hours, placing them on grids in the lab and further weighed as a function of time until they reached a constant weight.
Water uptake given in this paper were measured using capillarity absorption along the longitudinal axe. Only "longitudinal" water absorption were measured and reported in this study, as this measurement enables easy differentiation between different water repellent formulations.
Wood pieces were weighed and placed on metallic supports such as a small surface is in contact with water. The immersed part of wood pieces was adjusted at 2 mm during the entire test period. Samples were sponged with a paper and weighed after different contact time with water.

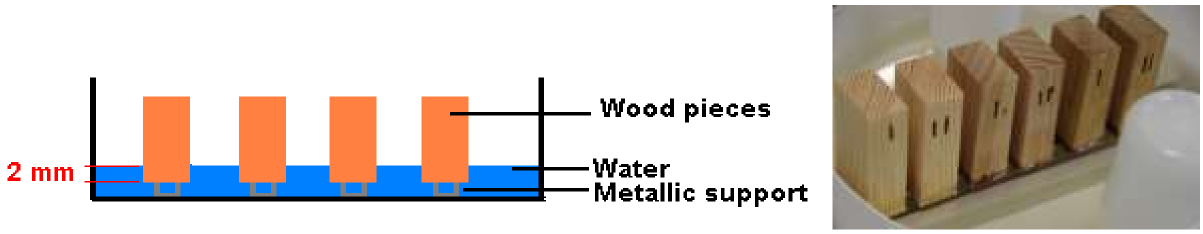

Figure 2 : experimental set up to measure "longitudinal water absorption".

All treated and untreated specimens showed higher water uptake in the longitudinal direction (than in the radial direction for example) due to the longitudinal orientation of the tracheids.

3. RESULTS

3.1 Application of water repellent by vacuum impregnation

Three commercial water repellents differing by not only the active material but also the delivery system, were used side by side to treat wood specimens by vacuum impregnation. A water soluble silane (SIL A), an emulsion of a mix of siloxane/silane/resin (EM A) and a microencapsulated siloxane polymer (MIC A) were used for vacuum impregnation. In the latter formulation, a siloxane polymer is microencapsulated in a silica shell formed by sol-gel process. Such microcapsules are solid and therefore cannot adapt their shape to penetrate into pores. The Table 1 hereafter gives the weight percent gain measured after vacuum impregnation. Despite the very different type of delivery system, no large differences of weight percent gain, for the different wood species and water repellents are observed.

Table 1: Weight percent gain after vacuum impregnation of wood with different water repellents.

WPG (%)	EM A	MIC	SIL A
Scots pine sap	1.10	1.13	1.17
Beech	1.09	1.50	0.97
Oak	0.43	0.46	0.40

The following graphs shows the weight gain (averaged value of three individual measurements) due to the water uptake (as % of the initial dry weight) plotted as a function of contact time with water or drying time. Wood specimens were placed into contact with water for 72 hours and then let for drying for the rest of the experiment duration.

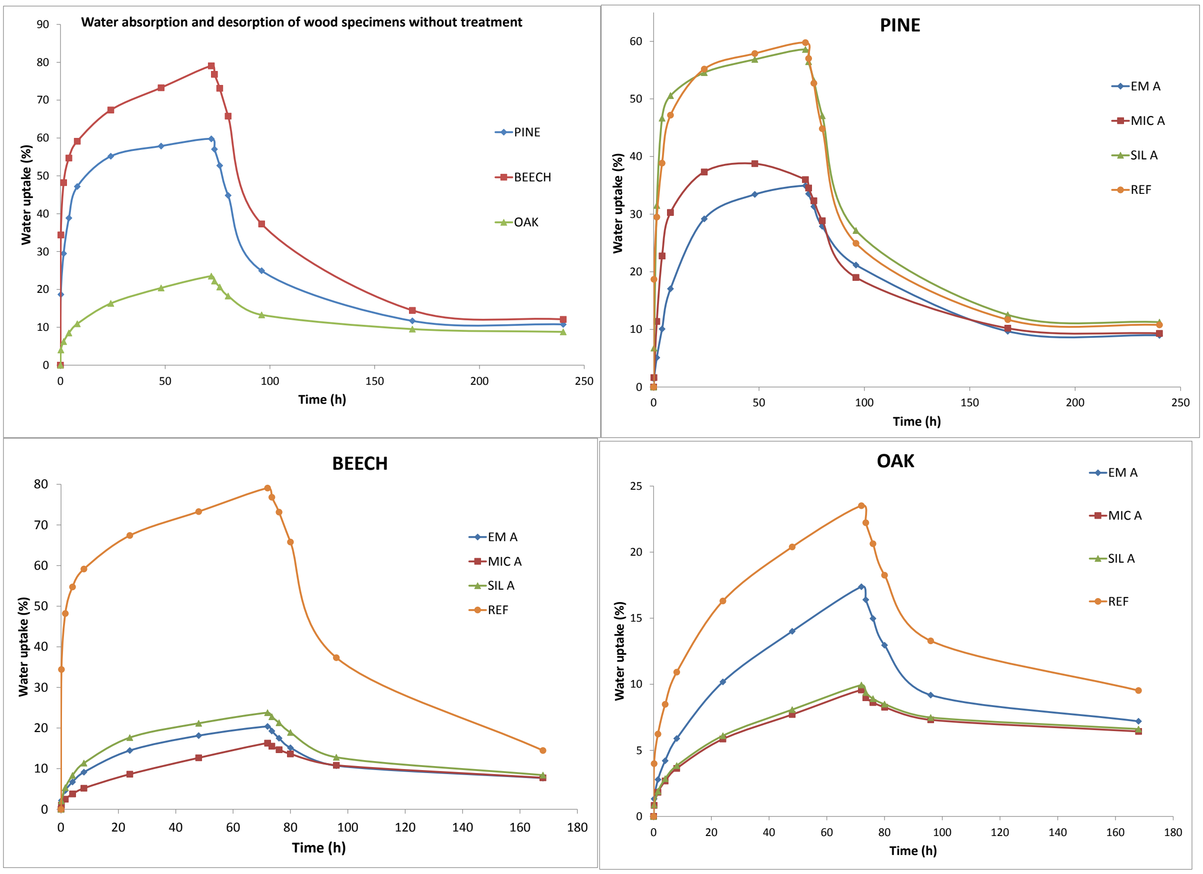

Figure 2: Water uptake (as a % of initial wood specimens dry weight) as a function of contact time with water and after 72h, as a function of drying time.

As the wood specimens were dried in an oven before the water uptake experiments, some adsorbed water was probably desorbed, leading to an artificially low initial weight. Weight obtained after the drying phase is therefore higher than the one at the beginning of the experiments.
It is clear that the use of different silicon-based water repellent reduces water penetration to different extend with different wood species. It can be observed that treatment of wood specimens with silicon-based water repellent does not slow down rate of drying, which was expected, as they are not film forming.
Treatment with the water soluble silane (SIL A) lead to some change of the wood specimen color (some color enhancement). It was also visuallly observed and measured (data not reported here) that leaching of extractables (probably tannins) from the wood specimens (especially oak specimens) during the water absorption test is much reduced when wood is treated with SIL A.

3.2 Application of water repellent by brushing

While vacuum impregnation nicely reproduces industrial processes, application of water repellent by brushing could relates to domestic use. Water repellents were applied by brushing on the different wood specimens.
The same water soluble silane (SIL A) and siloxane/silane/resin emulsion (EM A) were used. A cationic emulsion of an organofunctional siloxane was used as comparison (EM B). Also oil based formulation was prepared. It is based on the same resin used in EM A. The silicone resin was diluted in the same silane as in EM A to prepare formulation RES A.

Wood specimens were conditioned in the lab (25°C, +- 50% relative humidity). After brushing with water repellents diluted such as to reach 10% active content, wood specimens were dried for 7 days in the lab in the same condition before measurement of the “longitudinal” water uptake.
The following table gives the weight percent gain after application and after drying of a 10% active content water repellent dilution or straight silane/resin mix applied on the different wood specimens (average of 2 individual measurements).

Table 2: Weight percent gain after brushing different water repellents on wood specimens.

WPG (%)	SIL A	EM A	EM B	RES A
Scots pine sap	0.63	0.70	0.70	3.8
Beech	0.69	0.72	0.73	4.0
Oak	0.36	0.32	0.35	1.3

“Longitudinal” water absorption was calculated by measuring weight of wood specimens as a function of contact time with water.
The following graphs shows the “longitudinal” water absorption (as % of water uptake vs initial dry weight) after 48 hours contact time with water for the wood specimens treated by brushing with the selected water repellents.

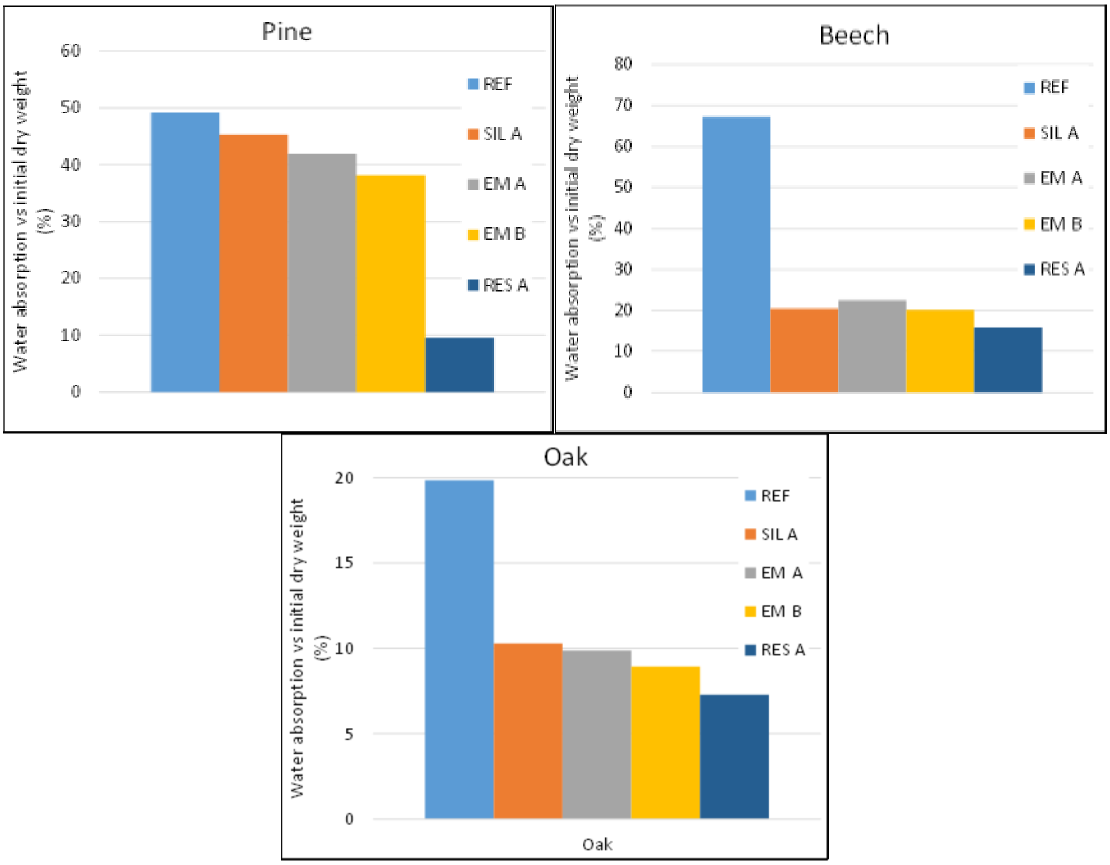

Figure 3: "Longitudinal" water absorption (as % of water uptake vs initial dry weight) after 48 hours contact time with water for the wood specimens treated by brushing with the selected water repellents.

Application by brushing does not enable the loading of large quantity of water repellent on the wood specimens. This minimize the efficiency of the water repellent treatment when applied on pine. Beech and Oak specimens are seemingly somewhat less sensitive on the quantity of water repellent applied to effectively minimize water penetration. It is probable that brushing leads to a higher concentration of active material close to the surface and can still enable an effective treatment at lower loading. No deep protection is however expected when water repellent is applied at the surface only. Brushing of silicone resin/silane mix strongly minimizes water penetration. "Oil based water repellent" can be considered as containing 100% of active content. Higher WPG is measured when neat/straight resin/silane blend is used which must lead to a higher concentration of the resin the surface of the wood specimens, leading to more effective reduction of water penetration. Contact angle of 2 µl water droplets placed on the large surface of the wood specimens were measured directly and 20 s after application with the help of a VCA optima XE device. The following Table 3 gives the contact angles of water droplets placed on the different treated wood specimens.

Table 3: Contact angles of water droplets placed on the different treated wood specimens.

Contact angle (°)	**PINE**		**BEECH**		**OAK**	
	t = 0s	t = 20s	t = 0s	t = 20s	t = 0s	t = 20s
REF	88	45	109	66	106	100
SIL A	107	92	108	101	106	100
EM A	128	126	140	140	126	122
EM B	125	120	136	117	126	117
RES A	113	109	126	126	101	79

An increase of contact angle of water droplets is obviously observed when wood is treated. However, there is no clear correlation between the contact angle of water droplets and the reduction of water penetration. This lack of correlation is known and further confirmed here.
This contribution shows that different product concepts (different water repellent active materials, different delivery systems) can be used as water repellent for wood. Water soluble active material or oil in water emulsion can be used for vacuum impregnation of surface brushing. Oil based formulation applied by brushing is quite effective, most presumably due to the high loading of active material on the wood specimens.
Impact of the treatment of wood by the water soluble silane (SIA A) and the two emulsions (EM A and EM B) on biological degradation and resistance to termite was assessed.

3.3 Protection against wood damaging fungi

All three water repellents tested in this study failed in providing long-term protection of wood against blue stain in real-use situation (outdoor exposure). However, the results obtained for in vitro experiments demonstrated that the products had an effect on the development of moulds and blue stain fungi, slightly reducing their growth (Kutnik *et al.* 2016).
The tests aiming at determining protective efficacy against basidiomycete decay fungi were the most conclusive. Among the three tested products, the cationic emulsion and water soluble silane significantly reduced mass loss caused by fungal degradation compared to the untreated controls. Water soluble silane and the cationic emulsion were both found to improve the resistance against fungal decay of Scots pine and beech to an extent comparable to the natural durability of European oak having a natural durability class ranging from 1 to 3 according to Brischke and co-authors (2013). Further artificial weathering tests are required in order to evaluate the suitability of the two water repellent formulations as wood protection products for outdoor above-ground use.

3.4 Protection against subterranean termites

In artificial situations of forced feeding, termites appeared to attack wood impregnated with the water repellents out of necessity, but could not sustain themselves and died after a few weeks. In situations of choice between different sources of food, which are more representative of real-life situations encountered by subterranean termites, they tended to avoid the wood treated with the water repellents.
Little damage and low mortality were recorded in the “choice” tests, demonstrating that termites were poorly attracted by wood treated with SIA A, which in turn resulted in indirect protection of the treated samples. On the other hand, the cationic emulsion resulted in low damage of wood and high mortality of termites for both test protocols.

3.5 Field testing of moisture dynamics

The continuous moisture measurement (CMM) set up as detailed in Figure 4, was first installed to assess the moisture dynamics of plywood (Van den Bulcke *et al.* 2009). This methodology was already used to assess modified wood (Van Acker *et al.* 2015) and now it has been used to follow a set of organosilicon treated specimens. Edges of the specimens were sealed. After installation in May 2015 a specific rain event at the end of August 2015 (Van Acker *et al.* 2016) and August 2016 which was selected to analyse major differences in Figure 5.

Figure 4: The continuous moisture measurement (CMM) set up.

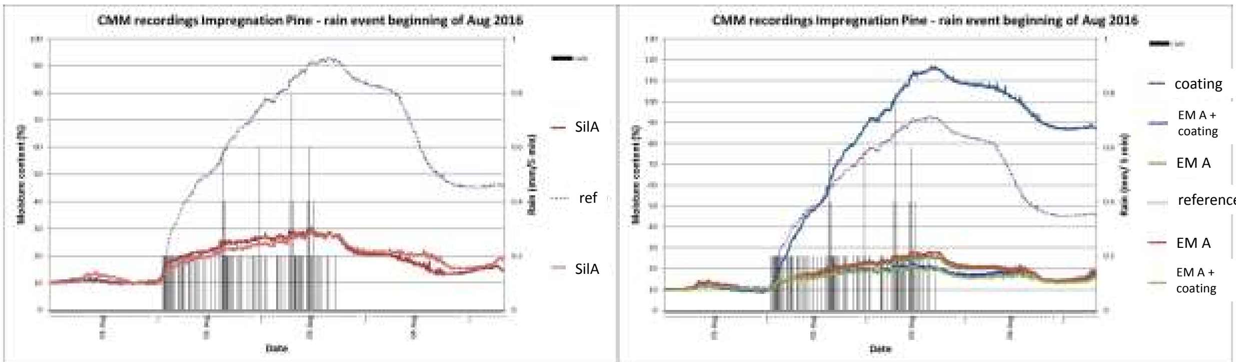

Figure 5: The continuous moisture measurement (CMM) of Scots pine sapwood treated with products SIL A and EM A during rain events end of August 2016.

Interestingly, continuous moisture measurements of specimens of Scots pine sapwood treated with water repellent SIL A and EM A (used as example here) are showing significant decrease of water absorption vs the reference specimens. Much smaller differences between treated and untreated specimens were found with oak specimens.

4. CONCLUSIONS

Silicon-based water repellents can be used to minimize water penetration into various wood species. Extend of reduction of water penetration depends on the treatment and on the specific wood species.
Continuous moisture measurement clearly demonstrates the reduction of water uptake, in "real life condition", especially with treated Scots pine sapwood.
Treatment of wood leads as well to reduced fungal degradation and to some extend to reduce degradation induced by termites.

5. ACKNOWLEDGEMENTS

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