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PROJECT FINAL REPORT

Grant Agreement number: 315425

Project acronym: WOOD-FLARETCOAT

Project title: Flame-retardant coatings based on nano-magnesium hydroxide, huntite and hydromagnesite for wood applications

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4.1 Final publishable summary report

Executive summary

WOOD-FLARETCOAT project, “Flame-retardant coatings based on nano-magnesium hydroxide, huntite and hydromagnesite” (Grant Agreement No 315425) had, as a resume, the objective of producing improved flame retardant coatings for wood products, through the development of non-halogenated flame retardant systems based on inorganic flame retardant nanofillers (nano magnesium hydroxide, huntite and hydromagnesite) functionalised with ROs and incorporated into several water born polymeric matrices, to constitute composites. Based on that idea different coating formulations were developed for wood materials for construction (both new buildings and restoration processes) and furniture, showing not only flame retardancy but also some more additional properties, such as antibacterial activity, enhanced scratch resistance or photocatalytic effect.

Since the selected inorganic flame retardants were insoluble in the polymer matrices to which were added, functionalization by coupling agents named peroxide reactive oligomers (ROs) was necessary with the aim of enhancing the compatibility between the filler and the matrix, thus avoiding undesirable effects such as water pick up and swell, poor dispersion and distribution and a reduction in physical properties of the composites.

With the aim of developing a family of multifunctional coatings able to provide the wood with some desirable properties apart from flame retardancy, several metal nano-oxides were incorporated into the polymeric matrices: ZnO and TiO_2 were found to provide antibacterial activity and photocatalytic effect.

During the first stage of the project, a wide range of flame-retardant fillers were prepared and characterized, as well as some batches of ROs. Some preliminary tests allowed the selection of the most promising fillers.

Then, a number of coatings were prepared at lab scale by incorporating the selected fillers into different polymeric matrices. The evaluation of the obtained coatings, both in terms of general properties and fire performance, led to a first selection of basic formulations.

Later, metal nano-oxides were incorporated into the mixtures with the aim of checking the provided special effects: scratch resistance, antibacterial activity and photocatalytic capacity were studied.

Once the best mixtures were chosen, semi-industrial lines able to produce both the fillers and the coatings were designed, assembled and optimized. Large batches of products were obtained very successfully. During the up-scaling of the processes, some modifications were performed on the final formulations and production procedures.

During the last stage of the project, the most interesting formulations obtained at semi-industrial scale were validated during demonstration process. The tested coating showed great applicability and final film quality, and provided the wood with a protection against fire when compared to untreated wood. In addition, techno-economical assessment showed that such coating could have very competitive price in the market. Last, a performed Life Cycle Analysis estimated that the environmental impact related to the production of this coating was very low.

Further information about WOOD-FLARETCOAT project can be accessed online at:
www.wood-flaretcoat.eu

Summary description of project context and objectives

Fire performance is one of the main obstacles to an increased use of wood in most countries. New European classification systems for fire performance have recently been agreed, but the national safety levels will remain, causing continued limitations in the use of wood products. In figures, fires in dwellings cause in Europe over 4.000 deaths and 80.000 diverse injuries per year. The cause of death is suffocation due to smoke in about two thirds of the cases, while burns result only in about one third of the fatalities.

When heated, wood burns by producing flammable volatiles that may ignite. To reduce flammability, wood is treated with flame retardants (FR) which drastically reduces the rate at which flames travel across the wood surface and reduces the amount of potential heat. However, some FR treatments may produce unwanted secondary side effects, such as increased moisture content, reduced strength, and increased potential to corrode metal connectors. In order to prevent these side effects, fire retardant treatments may improve the fire performance of wood products considerably through reducing ignitability, rate of heat release and flame spread.

Flame retardant (FR) additives are added to materials to reduce/eliminate the risk of fire and the commercial market for these additives is presently dominated by compounds containing halogens such as brominated flame retardants (BFRs) usually used in a combination with antimony oxides, which offer a high standard of flame retardancy such as V-0 accordingly to UL-94 and exhibit sufficient physical properties. However, the use of halogenated compounds has one major drawback, they increase the amount of smoke and toxic decomposition products evolved during polymer combustion, which are extremely persistent on the environment, threatening both air and water ecosystems. On the other hand, other flame retardants which are non-toxic and environmentally friendly require large amounts to be effective and also could cause a variety of health disorders, including cancer. Furthermore, the use of high content of some additives often imparts a detrimental behaviour or an undesirable appearance of the material treated, decreasing mechanical properties such as impact strength, elasticity or producing changes in colour, stiffness among others. Hence there is an urgent need for the design of new non-toxic FR materials (preferably obtained from renewable resources) to substitute/eliminate the use of halogenated FRs.

Inorganic flame retardants, and specially metal hydroxides such as magnesium hydroxide (MH) are very promising alternatives for replacement of BFRs, since they can provide flame retardant formulations that meet the standards for quite a few applications, produce combustion products with low opacity, low toxicity, and minimal corrosivity, are easy to handle and remain immobile in the composite, without blooming. Magnesium hydroxide constitutes effective flame retardant and harmless filler widely used in practice over the past few decades in polymeric materials, because of its high decomposition temperature, which allows its use in wood materials processed at temperatures in the range of 300° C or even above. There have been many investigations on the properties of polymer composites filled with $Mg(OH)_2$, the compromise between fire resistance and other basic properties such as mechanical behaviour being a key point. The most important drawback related to the use of this kind of FR is that the amount of product required to obtain the target flame retardancy is in general more than 50% of the formulations, thus involving important negative effects on other properties, such as mechanical strengths. The following equation represents the thermal decomposition of MH, occurred at 300-330º C and giving rise to inert solid and water vapor. The endotherm for this reaction is quoted at values between 1244 J g^{-1} and 1450 J g^{-1}.

$$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$$

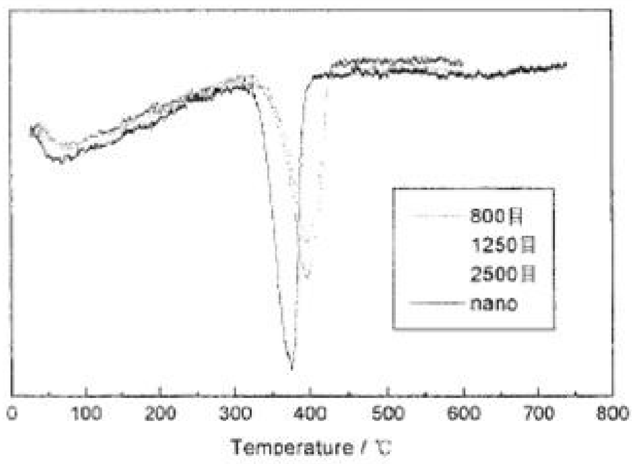
Apart from MH, a number of minerals showing flame retardant properties that could be of potential benefit in polymers have been identified. Each decomposes endothermically with the evolution of either carbon dioxide, water, or both. Among these minerals, hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) is the one that has probably seen most commercial interest. Hydromagnesite is naturally occurring in mixtures with huntite ($Mg_3Ca(CO_3)_4$). Its onset of decomposition is at a slightly higher temperature than that of MH and other metal hydroxides, making it suitable for polymers where metal hydroxides becomes unsuitable due to higher processing temperatures. Hydromagnesite has been shown to decompose endothermically releasing water and carbon dioxide over a temperature range of approximately 220–550º C.

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \rightarrow 5MgO + 4CO_2 + 5H_2O$$

This endothermic decomposition and release of inert gases gives hydromagnesite its fire retardant properties. Huntite also decomposes endothermically releasing carbon dioxide over a temperature range of approximately 450–800º C, as follows.

$$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2$$

Concerning to physical and flammability properties of a polymer filled with flame retardant additives, nanoparticle fillers are highly attractive since they can simultaneously improve both flammability and other basic properties. Researchers have discussed for a long time the influence of particle size of fire retardant additives in the properties and fire resistance of the composites concluding that the development of nanotechnology has led to a great number of kinds of nanoparticles which contribute to those improvements. In this sense, several studies have investigated different kinds of $Mg(OH)_2$ with different particle sizes, in order to observe the influence of this factor on several important properties of the composites, such as mechanical properties and fire resistance. As it is shown in the DTA curves shown below, the decomposition temperature of nanoparticles (380° C) is lower than that of microparticles (400° C), and the endothermic peak of nanoparticles is also relatively higher. What could be concluded from this is that nanoparticles decompose earlier than micro-$Mg(OH)_2$ and the endotherm of the nanoparticles is greater than that of micro-$Mg(OH)_2$. Nanoparticles can thus more effectively lower the flame temperature at the surface of materials and reduce the formation of combustible compounds.



Nanotechnology offers new ways to create materials promising a degree of property control not previously possible. For example, it has been demonstrated that carbon nanotubes can surpass nano-clays as effective FR additives if they form a jammed network structure within the polymer matrix, such that the material as a whole behaves rheologically like a gel and leads to the added benefit of enhancing the physical properties of nanocomposites relative to the polymer matrix. In the case of nanoparticles, as they have a very high surface area, when this surface is tailored functionalized, it can carry loadings of functional compounds, providing improved properties in the material.

In this context, the project *WOOD-FLARETCOAT* aimed to develop a new concept of flame retardant fillers to be incorporated into polymeric matrices giving rise to flame retardant coatings for wood applications, using functional nanotechnology. Different kinds of polymeric matrices were tested, all of them being water born systems which minimize air pollution in comparison with other kinds of matrices based on organic solvents. Several inorganic raw materials were used with the aim of obtaining a range of flame retardant fillers, having not only different nature but also different tailored surface and different particle size. Some batches of fillers were developed by modification of nano-magnesium hydroxide (NMH), obtained either by milling processes of $Mg(OH)_2$ or by hydration of nano-MgO. Other batches of fillers were developed by modification of huntite, hydromagnesite and mixtures of both minerals.

Since the selected inorganic flame retardants are insoluble in the polymer matrices to which will be added, functionalization by coupling agents named peroxide reactive oligomers (ROs) was necessary with the aim of enhancing the compatibility between the filler and the matrix, thus avoiding undesirable effects such as water pick up and swell, poor dispersion and distribution and a reduction in physical properties of the composites. ROs are a very broad new family of compounds which present multiple advantages as coupling agents in comparison to traditional ones. Among these advantages, it could be mentioned their possibilities to be easily tailored to fit a determined application.

With the aim of developing a family of multifunctional coatings able to provide the wood with some desirable properties apart from flame retardancy, several nano-metal oxides were incorporated into the polymeric matrices: ZnO, SiO_2, ZrO_2 and TiO_2 were tested. ZnO was expected to supply the coatings its antibacterial properties, ZrO_2, SiO_2 and TiO_2 were expected to provide scratch resistance properties and TiO_2 was expected to supply photocatalytic effect.

As a resume, the objective of the project *WOOD-FLARETCOAT* was to produce improved flame retardant coatings for wood products, through the development of non-halogenated flame retardant systems based on inorganic flame retardant nanofillers (nano magnesium hydroxide, huntite and hydromagnesite) functionalised with ROs and incorporated into several water born polymeric matrices, to constitute composites. Based on that idea different coating formulations were developed for wood materials for construction (both new buildings and restoration processes) and furniture, showing not only flame retardancy but also some more additional properties, such as antibacterial activity, enhanced scratch resistance or photocatalytic effect.

Description of the main S&T results/foregrounds

In order to reach the abovementioned objectives, the work to be developed during the project was divided into seven work packages (WP), six of them related to technical tasks and one of them devoted to management, dissemination and exploitation issues.

Each one of the WPs had specific technical objectives and, as the project was mainly planned according to a sequential path, the results obtained in each WP affected the following ones. In most cases, the WP concluded with a material selection, being the selected products the starting point for the next WP.

Below, a very short description of the objectives and main results related to each technical WP can be found. It is worth mentioning that, as expected, the number of selected formulations became reduced over the course of the project, as only a few of them met the demanding expectations marked in the last tasks, related to the up-scaling of the products and validation in real applications.

WP1. Definition of technical specifications and product planning

Objectives

To finely define the specific final applications of the products to develop and, therefore, the industrial requirements that must be fulfilled (regarding important aspects such as functionality, viscosity, etc) as well as the production processes that must be optimized during the project.

Main results

A definition of the most important specifications to be achieved by the products to be developed was obtained. Furthermore, the definition also provided a clear vision of the main materials to be used and their characteristics. Another important aspect defined in WP1 was the production processes to be carried out in the future WPs, identifying the main reactions and working conditions.

WP2. Labscale obtaining of Mg-based fillers and ROs to develop the flame-retardant fillers

Objectives

To obtain several batches of Mg-based fillers by means of milling processes of MH, hydration of nano-MgO and preparation of mixtures of huntite and hydromagnesite, as well as of several batches of ROs.

Main results

The selected flame retardant fillers were manufactured at laboratory scale through the different synthesis via defined in WP1, which involved milling, hydration and calcination processes, from $Mg(OH)_2$, huntite and hydromagnesite. Furthermore, the reactive oligomers required to improve the stability of the fillers in the matrices were also synthesised at laboratory scale.

During this WP, conditions of each one of the processes were optimized in order to obtain fillers showing the required properties, in terms of particle size, exfoliation, etc. At the end of the WP, nine different batches of Mg-based fillers were selected among the wide range of prepared products:

- A commercial $Mg(OH)_2$ batch (denoted as MH-3 within the project)
- A batch of $Mg(OH)_2$ obtained by milling of MH-3 (denoted as MH-3-m)
- A batch denoted as **MH-H_2O-1**, obtained by an optimized hydration method
- A batch denoted as **MH-H_2O-1-m**, which is in fact a product obtained by milling of MH-H_2O-1
- **H5**: (Huntite~ 88% and Hydromagnesite ~12%, Sibelco minerals)
- **LH-3**: (Huntite~ 20% and Hydromagnesite ~80%, Lkab minerals)
- **1290**: (Huntite~ 65% and Hydromagnesite ~35% Lkab minerals)
- **HYD-H5$_{550}$**: Obtained by treatment of H5
- **HYD-LH-3$_{500}$**: Obtained by another treatment of LH-3

In addition, three batches of reactive oligomers were successfully synthesized to be used as modifiers in further stages of the project:

- P(SSNa-co-GMA6)
- P(SSNa-co-GMA15)
- P(SSNa-co-GMA20)

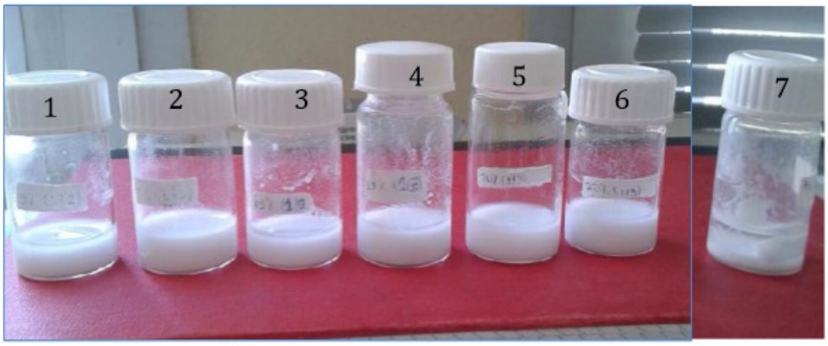
WP3. Labscale incorporation of the flame-retardant fillers into polymeric matrices and characterization of the obtained composites

Objectives

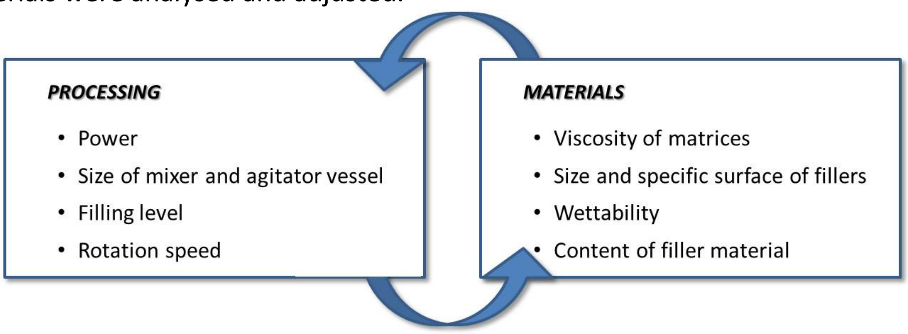
To obtain several batches of modified flame retardant fillers at labscale by modifying NMH, huntite and hydromagnesite; later incorporation of these fillers into polymeric matrices at labscale, characterization of the obtained coatings and subsequent application on wood substrates, followed by evaluation of properties and selection of formulations.

Main results

Reactive oligomers were used for Mg-based fillers dispersion stabilization. Optimization of various conditions was performed and a range of stable dispersions was obtained.



With the aim of obtaining homogeneous dispersions when incorporating flame-retardant fillers into polymeric matrices, several parameters of the processing and properties of the materials were analysed and adjusted.



Then, different fillers were incorporated into different matrices using several dosages. As a result, a wide range of coatings were obtained. The following tables summarize the prepared coatings.

Sample	Polymer dispersion	Filler	Filler content
1	Ecrothan 4075	-	0 wt%
2	Ecrothan 4075	MH-3m	20 wt%
3	Ecrothan 4075	MH-3	20 wt%
4	Ecrovin LV340eco	-	0 wt%
5	Ecrovin LV340eco	MH-3m	20 wt%
6	Ecrovin LV340eco	MH-3	20 wt%
7	Ecrovin LV340eco	MH-3	50 wt%
8	Ecrovin LV340eco	MH-H_2O-1	20 wt%
9	Ecrovin LV340eco	MH-H_2O-1	50 wt%
10	Ecrovin LV340eco	LH-3	20 wt%
11	Ecrovin LV340eco	LH-3	50 wt%
12	Ecrovin LV372	-	0 wt%
13	Ecrovin LV372	MH-3m	20 wt%
14	Ecrovin LV372	MH-3	20 wt%
15	Ecrovin LV372	MH-3	50 wt%
16	Ecrovin LV372	MH-H_2O-1	20 wt%
17	Ecrovin LV372	MH-H_2O-1	50 wt%
18	Ecrovin LV372	LH-3	20 wt%
19	Ecrovin LV372	LH-3	50 wt%

Evaluation of obtained coatings consisted basically on analysing the filler dispersion and the fire performance in terms of LOI, UL94 and micro calorimeter investigations. In summary, it was found that Mg-based fillers could be homogeneously distributed very well in aqueous polymer dispersions based on polyacetate, leading to the best flame retardancy. These coatings could be classified in the best UL94 category: V-0. When 50wt% of fillers was incorporated into the polyacetate-based dispersions, the Limited Oxygen Index as well as total heat release rate were significantly enhanced compared to the polyacetate-based coatings containing 20wt% of fillers.

Polymer matrix content (%)	Huntite H5 content (%)	Additive content (%)	P content (%)	Film quality [a]	LOI
			Ecrothan 4075		
100	-	-	0	+ + +	25.0±0.0
			Ecrothan 4075/Huntite H5		
50	50	-	0	+ + +	26.5±0.7
			Ecrothan 4075/Huntite H5/P(SSH-co-SSP(Ph)$_3$60)		
38.5	38.5	23	0.96	+ + +	27.5±0.7
			Ecrothan 4075/Huntite H5/ROs [P(SSNa-co-GMA20)]		
42.9	42.9	14.2	0	+ + +	30.0±0.0

Polymer matrix content (%)	Huntite H5 content (%)	Additive content (%)	P content (%)	Film quality [a]	LOI
			Ecrovin LV 340 eco		
100	-	-	0	+ + +	23.0±0.0
			Ecrovin LV 340 eco /Huntite H5		
50	50	-	0	+ + +	29.5±0.7
			Ecrovin LV 340 eco/Huntite H5/P(SSNa-co-SSP(Ph)$_3$50)		
37.2	37.2	25.6	0.94	+ + +	31.5±0.7
			Ecrovin LV 340 eco/Huntite H5/P(SSH-co-SSP(Ph)$_3$60)		
38.5	38.5	23	0.96	+ + +	31.5±0.7
			Ecrovin LV 340 eco/Huntite H5/ ROs [P(SSNa-co-GMA20)]		
44.0	44.0	2.0	0	+ + +	30.5±0.7
42.9	42.9	14.2	0	+ + +	37.8±2.5
39.3	39.3	21.4	0	+ + +	35.3±0.7

35.8	35.8	28.4	0	+ + +	35.0±0.0

Polymer matrix content (%)	*Huntite H5 content (%)*	*Additive content (%)*	*P content (%)*	*Film quality* [a]	*LOI*
		Ecrovin LV 372			
100	-	-	0	+ + +	22.5±0.7
		Ecrovin LV 372/Huntite H5			
50	50	-	0	+ + +	28.0±0.0
		Ecrovin LV 372/Huntite H5/P(SSH-co-SSP(Ph)330)			
46.35	46.35	7.3	0.52	+ +	32.0±0.0
		Ecrovin LV 372/Huntite H5/P(SSH-co-SSP(Ph)360)			
43.8	43.8	12.4	0.89	+ +	31.5±0.7
		Ecrovin LV 372/Huntite H5/ ROs [P(SSNa-co-GMA20)]			
42.9	42.9	14.2	0	+ + +	34.8±0.9
39.3	39.3	21.4	0	+ + +	34.7±0.6
35.8	35.8	28.4	0	+ + +	34.0±0.0

[a] +++: Excellent, ++: Medium, +: Low, Ø: No film

Very promising results were obtained, as in all cases the used additives improved the fire performance of the neat matrix, in particular when previous modification with ROs took place. This may be a strong indication of the compatibility enhancement between the filler and the matrix occurred when such kind of additive is used, which allows a good dispersion and a high fire performance.

The last task of this WP consisted of applying the coatings on wood substrates, in particular standard birch plywood, and evaluating their fire performance. The reaction to fire testing was performed in small scale and complemented by predictions of possible class according to the European system. The following tables show the results obtained during this evaluation.

Samples (1st batch)	Test results from Cone calorimeter, ISO 5660, at heat flux 50 kW/m^2		Possible Euroclass
Code	Time to ignition (s)	Heat Release Rate, First peak (kW/m^2)	
BB29	31	301	D
BB30	27	214	D
BB31	31	313	D
BB32	**27**	**185**	**D**
BB80	30	222	D
BB81	31	348	D
BB82	33	290	D
BB83	31	331	D
BB126	28	298	D
BB129	29	245	D
BB149	31	265	D
BB150	31	323	D
BB164	33	254	D
BB165	39	247	D
BB166	35	313	D
BB167	27	308	D
Untreated plywood (= standard substrate)			
Test 1	24	225	D
Test 2	28	216	D

Samples (2nd batch)	Test results from Cone calorimeter, ISO 5660, at heat flux 50 kW/m^2		Possible Euroclass
Code	**Time to ignition (s)**	**Heat Release Rate, First peak (kW/m^2)**	
311, 1 coat	18	231	D
311, 4 coats	21	179	D
314, 1 coat	25	249	D
314, 4 coats	18	256	D
317, 1 coat	23	292	D
317, 4 coats	20	256	D
318, 1 coat	24	210	D
318, 4 coats	**23**	**155**	**C/D**
320, 1 coat	31	272	D
320, 4 coats	17	244	D
321, 1 coat	20	219	D
321, 4 coats	26	203	D
Untreated plywood (= standard substrate)			
Test 1	24	225	D
Test 2	28	216	D

The coating systems studied so far indicated in most cases the same Euroclass as untreated wood, i.e. European reaction to fire class D. As a consequence, formulations and/or application systems had to be improved before continuing with the planned activities.

WP4: Labscale incorporation of additional functionalities into the composites

Objectives

The main objective of this WP was to obtain at labscale flame-retardant coatings with additional functionalities by incorporating several metal nano-oxides: ZnO to provide antibacterial properties, ZrO_2 and TiO_2 to improve scratch resistance and TiO_2 to supply photocatalytic effect. Obtained coatings were characterized following a range of methods and applied on wood substrates, so they were evaluated and the best ones were selected to be up-scaled.

Main results

A great number of coatings were prepared using the basic formulations developed during WP3, introducing metal nano-oxides to provide special properties. In addition, one more polymeric matrix (Vilacryl DS55K) was tested following recommendations from Loufakis, with the aim of improving the fire performance of the products.

Some of the prepared coatings showed very poor filler dispersion into the matrix, so they were improved by pre-dispersing the fillers in water before being added to the matrix. At the end, the following mixtures were obtained:

Sample	*Flame retardant filler*	*wt% ZnO*	*wt% TiO_2*	*wt% ZrO_2*
CO-MH3m-0	MH-3m	0	0	0
CO-MH3m-1	MH-3m	1	1	0
CO-MH3m-2	MH-3m	4	4	0
CO-MH3m-3	MH-3m	1	1	1
CO-MH3-0	MH-3	0	0	0
CO-MH3-1	MH-3	1	1	0
CO-MH3-2	MH-3	4	4	0
CO-MH3-3	MH-3	1	1	1
CO-LH3-0	LH-3	0	0	0
CO-LH3-1	LH-3	1	1	0
CO-LH3-2	LH-3	4	4	0

Code	*Matrix*	*Fillers*	*%*
CO-MH3m-11	Ecrovin LV340eco	MH-3m/ZnO	20/8
CO-MH3m-12	Ecrovin LV340eco	MH-3m/ZrO_2	20/8
CO-MH3m-13	Ecrovin LV340eco	MH-3m/TiO_2	20/8
CO-MH3m-14	Ecrovin LV340eco	MH-3m/Phosphorous compound	20/10
CO-H5-m1	Ecrovin LV340eco	H5-m/ZnO	20/8
CO-H5-m2	Ecrovin LV340eco	H5-m/ZrO_2	20/8
CO-H5-m3	Ecrovin LV340eco	H5-m/TiO_2	20/8
CO-H5-m4	Ecrovin LV340eco	H5-m/Phosphorous compound	20/10

	Matrix		**Matrix/ Huntite ratio**
	Type	**Weight (g)**	
BB148	EcrovinLV340eco	21,6	1/1
BB218	Vilacryl DS55K	7,0	1/6
BB224	Vilacryl DS55K	30,15	1/1,7
BB225	Vilacryl DS55K	13,8	1/2,73

After analysing fire results, it was clear that the addition of metallic nano-oxides did not reduce the efficiency of the flame-retardant fillers. In some cases, such addition led to even better fire performance results. The following table shows part of the obtained results:

Code	Composition	*LOI*
	Ecrovin LV372	
400	***0 wt %***	20.4
406	***20 wt% MH-3m***	25.1
451	***20 wt% MH-3m + 8 wt% ZnO***	25.5
453	***20 wt% MH-3m + 8 wt% ZrO_2***	23.9
452	***20 wt% MH-3m + 8 wt% TiO_2***	24.7
	Ecrovin LV340eco	
316	***0 wt %***	19.3
315	***20 wt% MH-3m***	22.9
351	***20 wt% MH-3m + 8 wt% ZnO***	25.8

353	***20 wt% MH-3m + 8 wt% ZrO_2***	25.9
352	***20 wt% MH-3m + 8 wt% TiO_2***	23.8

Regarding additional properties, several tests were performed on the coatings:

Scratch resistance

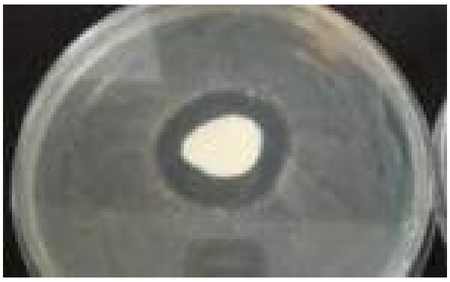
The addition of nano-oxides to the selected formulations of flame-retardant coatings improved the scratch resistance, the nature of the metallic oxide not affecting. The coating that best results presented in the scratch resistance test was CO-MH3-m13.

Antibacterial activity

A complete study was performed on those coatings showing suitable fire performance and good filler dispersion, evaluating the antibacterial with three different mircrobes:

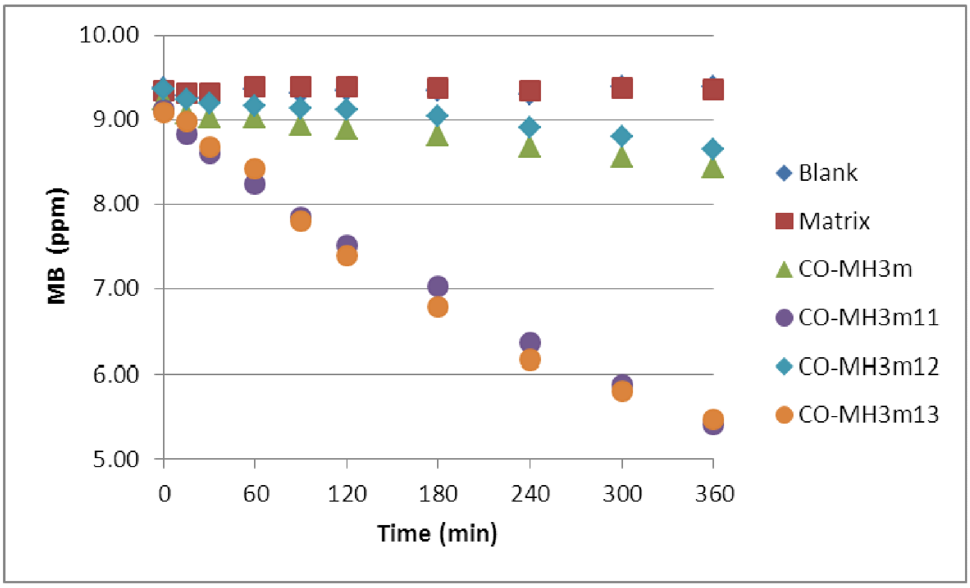
- Pseudomonas Aeruginosa (bacteria)
- Escherichia Coli (bacteria)
- Aspergillus Niger (fungus)

ZnO was found to be the main product providing antibacterial capacity to the coatings, which, in general, were effective with all the tested microbes The following picture shows one sample with antibacterial activity, represented by the clear zone around the powder.



Photocatalytic effect

Photocatalytic activity was measured by means of the degradation that each coating could cause on methylene blue molecules. The graph below shows the results obtained for the most efficient coatings:



Maximum degradation rate occured for the CO-MH3-m11 and CO-MH3-m13 coatings, due to the presence of TiO_2 and ZnO nanoparticles.

Application on wood specimens

Once the properties of the products were evaluated, the coatings were applied on wood substrates with the aim of analysing their real performance. The reaction to fire testing was performed at lab scale according to the cone calorimeter ISO 5660 at the heat flux 50 kW/m^2 and complemented by predictions of possible reaction to fire class according to the European system. The following tables summarize the obtained results; it can be seen that several coatings reached Euroclass C or even B, thus achieving the initial goal of the project.

Samples from Lurederra	Test results from Cone calorimeter, ISO 5660, at heat flux 50 kW/m^2		Possible Euroclass
Code	Time to ignition (s)	Heat Release Rate, First peak (kW/m^2)	
CO-MH3-m16	26	207	D
CO-MH3-m17	25	172	C/D
CO-MH3-m18	29	183	C/D
Untreated plywood (= standard substrate)			
Test 1	24	225	D
Test 2	28	216	D

Samples from FORTH	Test results from Cone calorimeter, ISO 5660, at heat flux 50 kW/m^2		Possible Euroclass
Code	Time to ignition (s)	Heat Release Rate, First peak (kW/m^2)	
BB148	31	158	C
BB218	**36**	**125**	**B**
BB224	31	287	D
BB225	36	258	D
BB260	31	160	C
BB261	**37**	**137**	**B**
BB262	**32**	**143**	**B**
BB263	24	150	C
BB266	31	177	C/D
BB267	30	156	C
Untreated plywood (= standard substrate)			
Test 1	24	225	D
Test 2	28	216	D

Samples from FORTH	Test results from Cone calorimeter, ISO 5660, at heat flux 50 kW/m^2		Possible Euroclass
Code	Time to ignition (s)	Heat Release Rate, First peak (kW/m^2)	
330, 1 coat	28	266	D
330, 4 coats	20	245	D
331, 1 coat	28	251	D
331, 4 coats	23	222	D
332, 1 coat	27	234	D
332, 4 coats	27	275	D
333, 1 coat	26	263	D
333, 4 coats	25	240	D
Untreated plywood (= standard substrate)			
Test 1	24	225	D
Test 2	28	216	D

WP5: Upscaling of the processes

Objectives

The objective of this WP was to obtain at semi-industrial scale those products selected during WP4 (both flame-retardant fillers and flame-retardant coatings). Predicted ranges were 1-2kg for the fillers and 20-50kg for the coatings. A detailed analysis of technical problems related to processes and products when upscaling from laboratory level to industrial scale was performed.

Main results

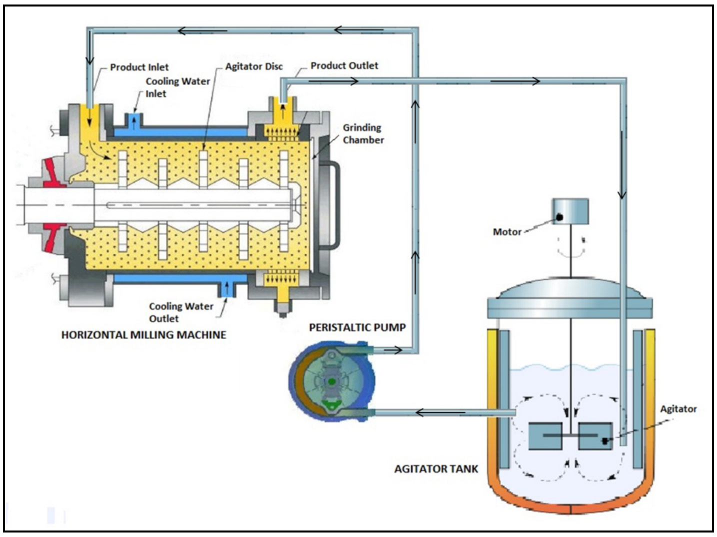
Production of fillers

Two different fillers were selected during WP4 to be produced at large scale: MH-3m, obtained by milling process, and H-5m, obtained by a process of calcination and hydration. So, it was necessary to study the design of semi-industrial lines able to produce such amounts.

The equipment used in this semi-industrial line of milling is the following:

- Horizontal milling machine
- Milling spheres
- Circulation system
- Storage tank
- Agitator

So, different options for each one of the elements were evaluated with the aim of choosing the most interesting ones.



In order to get a reproducible milling process and thanks to previous studies, the following five parameters were established:

- Solute-to-solvent weight ratio
- Grinding beads filling rate
- Milling temperature
- Rotation speed of agitator
- Flow velocity of circulating system

The milling time was optimized in order to get the desired particle size, 70 minutes being the selected time.

For the production of H-5-m, it had to be considered that calcination at an industrial scale can be carried out in conveyor belt furnaces, which allow control of the gaseous atmosphere and temperature profile during calcination. The production capacity is defined by the belt width and the residence time, which is related to belt speed and heated length. Heating may be either electrical or gas. An example of a conveyor belt furnace is given below.

Hydration of the resulting H-5m material should preferably take place soon after production to avoid any carbonation by atmospheric CO_2. It can be carried out at suspension concentrations up to 30-35 wt% and there is no need for separation of the final solids from the suspension, since this can be used directly in subsequent steps.

The controllable process parameters considered in the production of H5-m mineral were six:

- H5 amount per batch
- Calcination temperature
- Calcination time
- Air flow
- Hydrolysis time
- Hydrolysis temperature

Production of coatings

Coatings were produced at semi-industrial scale using the following selected components, based on the labscale coating showing the most promising Euroclass (B): B218.

- Matrix: the chosen matrix was VILACRYL DS55K, which revealed the best fire performance results in the previous WP.
- Flame-retardant fillers: three different products were selected: huntite (H-5), H5-m and MH-3m.
- Reactive oligomer: (P(SSNa-co-GMA20)), in order to improve dispersion.
- Metal nano-oxides: taking into account previous results, two types of nano-oxides were selected for this purpose: ZnO and TiO_2.

It has to be noticed that only one filler was used in each coating. However, nano-oxides were used in combination, as together they led to great results in terms of additional properties.

Machinery options for the semi-industrial production of coatings were analysed: agitation system, circulation system, reactors, etc. Final coatings showing great dispersion and the desired properties had to be obtained, both in terms of possibility of application and final performance.

During the optimization of the production conditions, some additives commonly used in the paint industry were incorporated into the formulations, as they were needed in order to obtain good processability and appropriate film quality.

At the end of this activity, three semi-industrial coatings were obtained. The following table shows the main characteristics of such coatings.

	Coating Hu	Coating Hu-nox	Coating MH-m-nox
Ph	**9,8**	**10,8**	**10,8**
Density	**1,21 g/cm^3**	**1,05 g/cm^3**	**1,13 g/cm^3**
Viscosity,23ºC	**18200cP**	**20300cP**	**5870 cP ****

Opacity on paper card *	**95,9%**	**95,3%**	**88,8%**
Whiteness CIE	**87,1%**	**77,9%**	**89,5%**
Solids in the oven 125ºC	**38,7%**	**34,1%**	**41,4%**
Gloss 60º	**3,4**	**2,3**	**2,3**
Gloss 85º	**21,5**	**2,4**	**7,0**

WP6: Regulatory study and techno-economical assessment

Objectives

The main objectives of this WP were, on the one hand, to demonstrate the coating materials in real wood applications and, on the other hand, to perform a complete techno-economic analysis of the developed products.

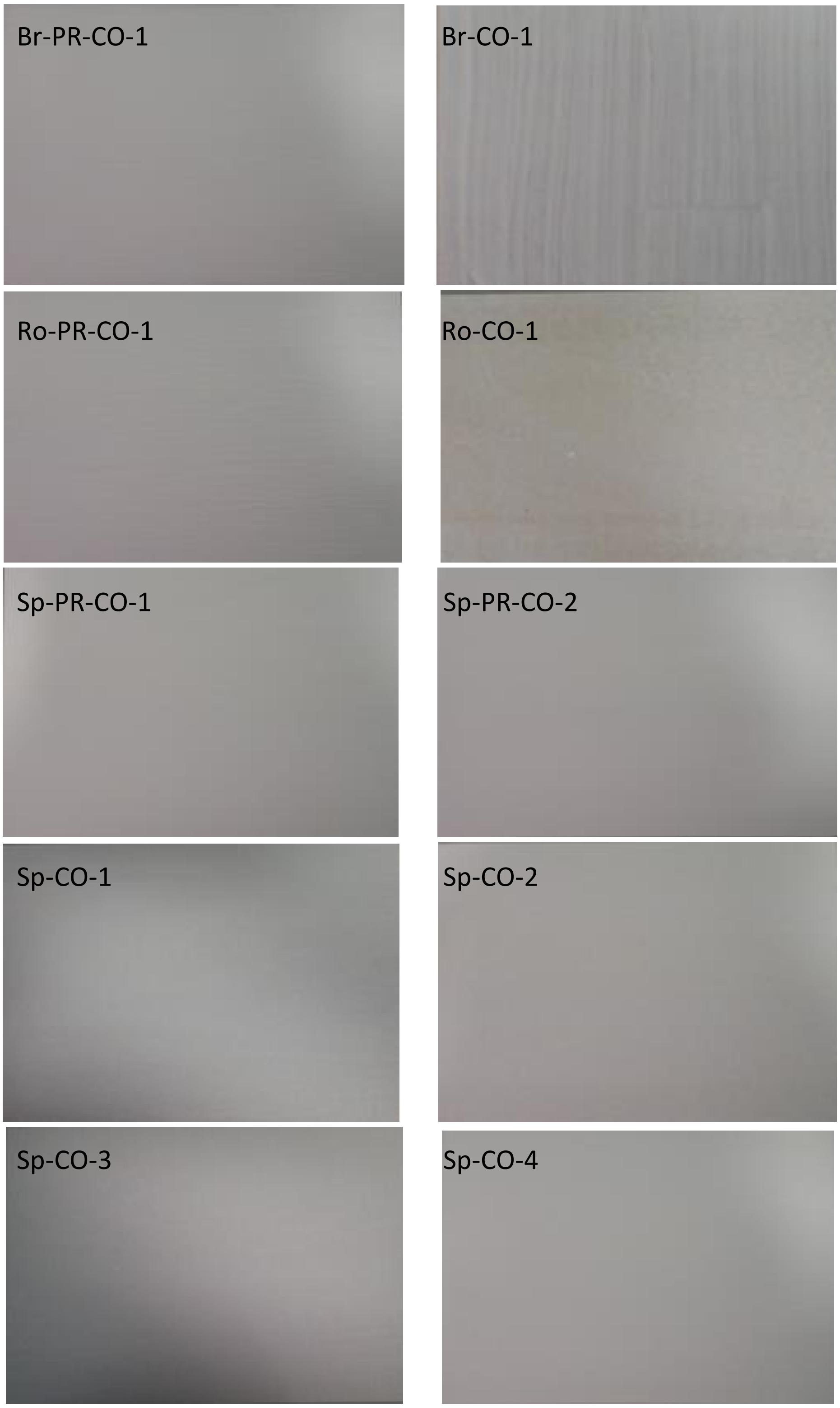
Main results

Application system

Three different application techniques were tested during validation stage: brush, roller and conventional spray. All these techniques were used to apply the coating directly on the plywood specimens and also to apply primer and, then, coating on plywood pieces. The table below summarizes the evaluated applications.

Specimen	Application type	Primer		Coating	
		Wet applied (g/m^2)	Dry applied (g/m^2)	Wet applied (g/m^2)	Dry applied (g/m^2)
Br-PR-CO-1	Brush	405	154	210,6	49,2
Br-CO-1	Brush	x	x	206	49,9
Ro-PR-CO-1	Roller	327		197,1	27,0
Ro-CO-1	Roller	x	x	188	26.4
Sp-PR-CO-1	Spray	148,6	61,9	519,3	163,2
Sp-PR-CO-2	Spray	181,1	79,0	420,4	123,9
Sp-CO-1	Spray	x	x	156,6	85,4
Sp-CO-2	Spray	x	x	248,1	111,3
Sp-CO-3	Spray	x	x	432,4	231,8
Sp-CO-4	Spray	x	x	579,7	277,0

The following figure shows the surface finish of these treated woods.



It can be observed that all the treated plywood specimens showed suitable film quality. For each one of the application methods, some parameters (such as the optimal amount of coating or the number of layers) were adjusted, thus giving rise to a range of application possibilities. The specific requirements of each concrete work will lead to the selection of the technique. It is worth mentioning that all the technical parameters related to the spraying by pressure were optimized for both primer and top coating. In addition, taking into account the characteristics of the products observed during the tests, some technical recommendations were done for the application in large areas using airless system.

Fire performance

The tested final coating (based on B218 coating formulation) was tested according to EN13823 SBI standard in order to obtain the Euroclass. It has to be noticed that the coating B218 was predicted to achieve a B Euroclass classification when applied over playwood specimens.

The following table and figure show the results obtained during this test.

	Test results from SBI, EN 13823, for final coating			Euroclass EN 13501-1 *
Product	FIGRA (W/s)	THR (MJ)	TSP (kW/m^2)	
Ordinary plywood	570-588	19,5-23,1	36-61	D-s2,d0
Coating Hu	252-315	26-28	18-26	D-s1,d0
Coating Hu-m-nox	232	25	20	D-s1,d0
Coating MH-m-nox	161-178	18,9-19,4	22-21,1	D-s1,d0

FIGRA Fire Growth Rate, THR Total Heat Release, TSP Total Smoke Production
** Limits for Class (Euroclass) C-s1,d0 is FIGRA 250 W/s, THR 15 MJ, TSP 50 m^2*
Limits for Class (Euroclass) B-s1,d0 is FIGRA 120 W/s, THR 7,5 MJ, TSP 50 m^2

As can be seen in the table above, the coating MH-m-ox achieved 2 of 3 parameters for Class C-s1,d0 according to classification standard EN 13501-1. Only parameter THR was not fulfilled.

A fire retardant coating must delay the ignition and provide a good fire protection so that the heat release during the whole test is low. If such premises are complied, a suitable fire performance is considered to be achieved. The Wood-FlaretCoat final coating delayed the ignition but the supplied fire protection was not enough to reach the target Euroclass, although a clear improvement when comparing to untreated wood was obtained. The formulation was proved to have the potential to reach even Euroclass B (already achieved at laboratory scale), so slight modifications in the application system, formulation dosages, some parameters of the used equipment or even the amount of applied coatings will be performed in order to optimize the procedures and obtain the desired Euroclass. As aforementioned, only one of three parameters has to be slightly increased to achieve this goal.

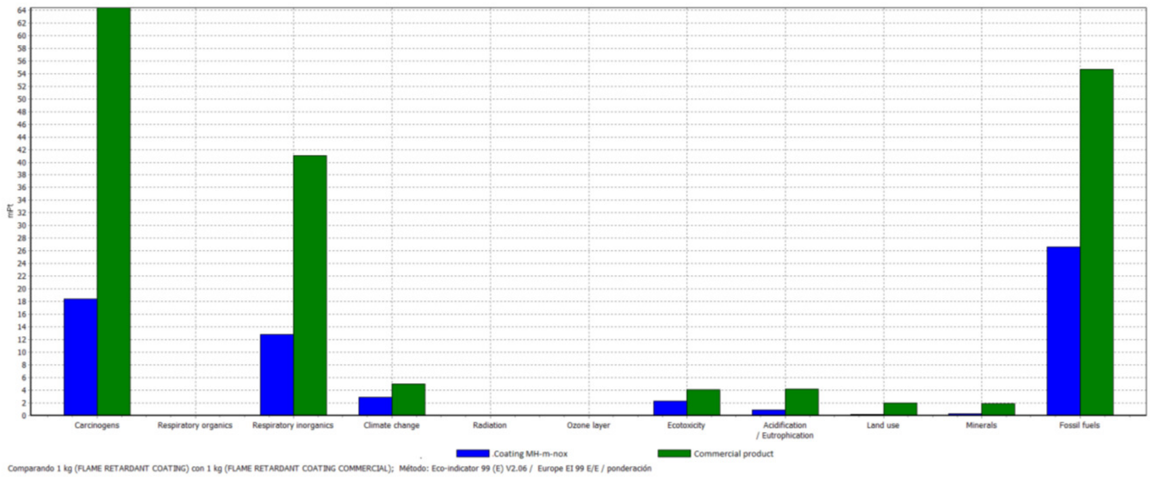
Colour

Some investigations were carried out in order to obtain coatings showing the same colour than wood pieces, by incorporation of a dye named Nogalina, specifically designed to be applied to wood materials. Both primer and coating acquired the desired appearance when some drops of product were added, as can be observed in the following figure.

These results supposed a great advantage, as this compatibility between developed coatings and Nogalina allow the use of the WoodFlaretCoat products in a wide range of applications in which a white appearance would be a problem.

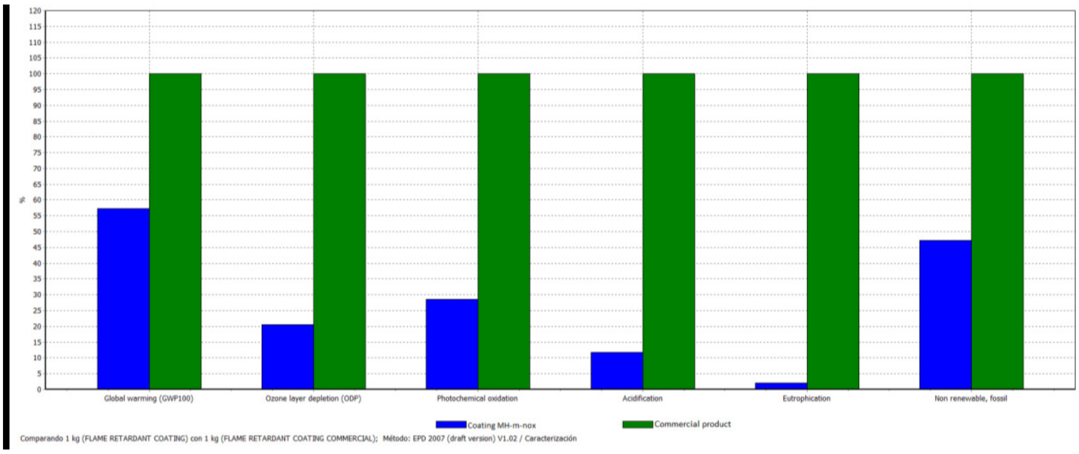
Life Cycle Analysis

A Life Cycle Analysis was performed on the Wood FlaretCoat coating, with the aim of checking the environmental impact related to the production of 20kg of such coating. In addition, a competitor product was also analysed with comparative purposes.



It was observed that the commercial product had higher environmental impact than the product developed in Wood-FlaretCoat project : 0,177 eco-Pt value for the commercial product and 0,065 eco-Pt value for the developed coating.

In addition, a comparative study of the amount of CO_2 equivalent for each product was carried out.



Such analysis showed that commercial product was more polluting than the one developed in the project. A total quantity of 1,24 Kg of CO_2 equivalent was produced by commercial product in contrast to 0,71 Kg of CO_2 equivalent obtained for the Wood FlaretCoat coating.

Techno-economical evaluation

In order to check the real possibilities of the developed product in the market, a complete economical assessment was performed with the aim of calculating the final price to be offered to potential clients.

Taking into account all the factors affecting the final cost of the coating (raw materials, energy consumption, labour time or profits, among others) the price of the product was calculated. Then, the yield of the product according to tests performed during validation stage was considered with the aim of determining the price of treating 1m^2 of wood. The same calculation was done for two competitor products, results being very promising: the obtained price for the product developed in the Wood FlaretCoat project was **8,41€/m^2**, while the price of other commercial products was in the range of 5,5 - 10,9€/m^2. So, the developed coating has very competitive price, especially taken into account that it offers not only flame-retardancy but also other interesting technical properties: antibacterial activity and photocatalytic effect.

Potential impact and main dissemination activities and exploitation of results

The project WOOD-FLARETCOAT intends to fully transfer the results obtained into industrial application, counting to that purpose with industrial companies interested in the subsequent exploitation of the products developed in the project. The Consortium of the project counts with 6 SME companies covering all the steps of the final device development and with direct benefit in the project.

WOOD-FLARETCOAT Project is expected to contribute to improve the competitiveness of the participants by several results that already are or are expected to be commercially valuable and exploitable in a short time:

- Increased share on the market of ROs and derivatives
- Increased share on the market of flame retardant fillers based on nano-magnesium hydroxide (NMH), huntite and hydromagnesite
- Increased share on manufacturing flame retardant coatings for wood applications
- Increased share on flame retardant treatments for wood applications (new construction buildings and restoration).
- New business opportunities for the applications of the developed coatings beyond wood sector.

- Increased knowledge on the production and application of flame retardant coatings
- Knowledge transfer from fundamental research into technically feasible and cost effective products and treatments.

Final results of WOOD-FLARETCOAT project are the obtainment of intermediate (ROs and derivatives and flame retardant fillers based on NMH, huntite and hydromagnesite) and final products (flame retardant coatings with additional functionalities) as well as treatments based on them for wood applications, although further applications beyond wood sector will be also considered.

The worldwide consumption of flame retardants amounts to around 2 Million tons a year. According to a 2012 market study of Townsend, the consumption of flame retardants will continue to grow at a global annualized rate of 4-5%. In 2013, more than 2 million tonnes of flame retardants were consumed worldwide and the market research institute Ceresana forecasted revenues of approx. US$7.15 billion to be generated in 2021.

This growth trend implies the reinforcement of the European chemical, coating production industry and internal and external wood industry, and thus in the creation of new jobs. The developments accomplished within WOOD-FLARETCOAT Project are expected to require setting up new facilities, therefore promoting employment. Also jobs, in which multidisciplinary skills are required, such as polymer engineers, chemists, production experts or skilled workers among others, will be enhanced.

The results of the project will also have a positive impact over environment, since they allow replacing halogenated and other substances, toxic in nature and with high environmental impact, by metal hydroxides, which are much more environmentally sound. In this sense, the impact on health and safety is also very positive, since the elimination of toxic components and halogenated flame retardants, will lead to a reduction in the fire effects, in the risk of smoke generation and in the percentage of dead by suffocation due to smoke. Although this issue would require deeper analysis, in principle the high percentage of inorganic components used highly reduces the adverse effects of smoke generated during combustion of different components developed.

Furthermore work developed and products obtained in WOOD-FLARETCOAT Project could be also taken as a starting point for new research and development activities in the field.

Dissemination activities and exploitation of results

During the development of the project WOOD-FLARETCOAT innovative end-user products and different exploitable results were obtained as shown in the table below:

Exploitable knowledge	**Exploitable product (s)**	**Sector (s) of application**	**Timetable for commercial use**	**Patents or other IPR protection**	**Owner & Other partner (s) involved**
Characteristics and conditions of ROs production	ROs	Composites production	Three years	No patents	Loufakis Eurochem
Characteristics and conditions of flame-retardant fillers production	Flame-retardant fillers based on NMH, huntite and hydromagne site	Coatings for different substrates (wood, plastic, stone, metallic surfaces, etc.) Different materials showing flame retardancy (e.g. construction materials)	Three years	No patents	Loufakis

Characteristics and conditions of flame-retardant coatings (with additional functionalities) production	Flame-retardant coatings	Wood structures and wood pieces, for building sector and restoration processes Structures and pieces based on other materials: stone, plastic, metals, etc.	Three years	No patents	Loufakis
Characteristics and conditions of flame-retardant coatings (with additional functionalities) application	Flame-retardant treatment with additional functionalities	Building sector Restoration market	Three years	No patents	Humichem Ingarp Ochoa

The use of this exploitable knowledge is regulated by the Exploitation Agreement prepared and discussed among partners.

Organizations belonging to the Consortium are doubly important as dissemination agents, since they are potential users of the project results themselves and they also represent the so-called influencers, being thus a natural channel for the dissemination of the project and the results to other potential users.

In the chart below an overview of the role of each participant in the project is presented.

Partner	Type	Area of Research or Business Activity	Specific role in the market
Lurederra	RTD	Main RTD fields: design, production and modification of tailored nanoparticles, incorporation into different matrices to obtain specific products.	Coordination of WOOD-FLARETCOAT project. Development of a range of modified flame-retardant fillers (based on NMH). Life Cycle Analysis. Offer of achieved knowledge to different companies
Humichem	SME	Company with great expertise in a variety of methods for the application of treatments on wood substrates, particularly for restoration processes.	Definition of technical specifications and product planning. Validation of the final coatings in real applications. Incorporation of the developed coatings (showing a range of functionalities) into its products' catalogue, to be applied on wood substrates from different clients, restoration processes being the main focus.
Ingarp	SME	Specialized in the industrial application of coatings to wood substrates in building field	Definition of technical requirements. Validation of the obtained coatings in real applications of building sector. Offer of such products to the wood building market.
Loufakis	SME	Industrial production of	Participation in the definition of materials and

		chemicals, such as polymers with controlled properties and finished products as coatings in 1.500kg batches	production processes. Industrial production of flame-retardant fillers and coatings. Industrial production of RO from 600kg to 8000kg batches. Consultancy for industrial production of flame-retardant fillers and coatings. Co-operation with Greek manufacturers of Huntite for the production of the special flame-retardant fillers. Introduction of the developed products in the market together with portfolio of water-based binders used in the formulations.
Eurochem	SME	Company expert in Chemistry and Chemical Engineering	Contribution in product planning. Production of modifiers. Expansion in the composites market by the introduction of such products.
Adigest	SME	Main activity line: consultancy for new materials, focusing on sustainability, safety and Life Cycle Analysis	Complete regulatory analysis of the developed products, including safety and environmental points of view. Offer to companies of consultancy services including knowledge acquired during the project: nanotechnology and fire performance.
Forth	RTD	Knowledge in the production and modification of fillers and execution of fire performance tests	Development of a range of modified flame-retardant fillers (based on huntite and hydromagnesite) Fire retardancy tests. Characterization of both lab & up-scaled batches. Synthesis of new polymeric reactive oligomers (RO).
IPF	RTD	Expertise in the formulation, production and characterization of polymer-particle nanocomposites	Incorporation of fillers into matrices at laboratory scale. Characterization of the products. Participation in the selection of formulations. RTD offer to different companies.
SP Trätek	RTD	Main RTD field: application of coatings on substrates (specially wood) and deep characterization of treated materials	Participation in the definition of final products. Laboratory scale application of coatings on wood substrates. Characterization. Reaction to fire tests for developing and classification. Durability of reaction to fire tests. RTD offer to different companies.
Ochoa	SME	Expert company in the design, production and optimization of tailored	Contribution in the definition of final products and processes.

		machinery for industrial processes, application of coatings being one of the main lines	Analysis of final products and application possibilities. Industrial application of coatings and optimization of equipment and involved parameters. Participation in validation stage. Incorporation of the coatings into the range of products offered to its clients. Expansion in the wood market.

Dissemination actions have been executed in order to promote the work accomplished during the WOOD-FLARETCOAT Project, its goals and achievements.

These activities involved among others:

- Participation in leading trade shows: in this section it is worth mentioning the participation of WOOD-FLARETCOAT Partners in the 11^{th} International Conference on Nanosciences & Nanotechnologies (NN14), in the 5^{th} International Symposium in Timber Architecture and Construction (EGURTEK), in the 10^{TH} Hellenic Polymer Society Conference (10-HPSC), the 31^{st} International Conference of the Polymer Processing Society (PPS-31) or in the V International Seminar of Nanoscience and Nanotechnology.

- Organization of a workshop and a training session: a virtual workshop on industrial production of new flame-retardant coatings & applications was organized and attended by every partner of the Project. In addition a training session for the SMEs was also organized, in which theoretical information was provided regarding physical properties of developed coatings and techniques to be used for application. Also a practical training on preparation and application of the coatings on plywood and oak and pine wood was carried out, all that followed by a fruitful discussion about possibilities of improvement and remarks on the quality achieved.

- Publications: besides presenting the results in prestigious conferences, publications in Annual Reports and Newsletters of the members of the consortium and on the Annual Report of the Spanish Network of Technological Centres (FEDIT) were done.

- Set-up and maintenance of a project website: during this second period the public part website www.wood-flaretcoat.eu was periodically updated with news and documents. Similarly the private part was used as an internal communication tool for the members of the Consortium to share reports, deliverables, etc.

- Video: a video showing most significant work performed within the project was developed and uploaded to both the Youtube channel of the Coordinator and to the public part of the website. https://www.youtube.com/watch?v=9fNB1fr_vUw.

- Presentations to small groups of interested parties: contacts with companies belonging to sectors such as wood, flame-retardant producers, painting or chemistry, were established. During these meetings the dissemination material generated was used, including the A4 Poster, the triptych leaflet or the brochure among others. It is worth mentioning the great interest shown by most of them on the project developments and results, as well as on future prospects.

- Networking: networking activities were also carried out. Concretely partners contacted project ENFIRO, focused on the substitution of brominated flame retardants, and REACTAFIRE, devoted to develop an advanced coating system using innovative materials which will accelerate the charring of wood and help to improve the structural fire protection. As WOOD-FLARETCOAT, these two projects are also funded by FP7.

Address of the project public website

www.wood-flaretcoat.eu