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4.1 Final publishable summary report

4.1.1 Executive summary

The main objective of NANOPIGMY project is to develop multifunctional ceramic pigments by applying nanotechnologies to commercial pigments. NANOPIGMY project seeks to produce cost-efficient multi-functional ceramic pigments with more functionalities than color to provide the automobile and construction materials with the required functionalities through the use of these nanotechnology-based pigments, thus avoiding changes in manufacturing processes. Specifically, they look for:

- **PIGMENT 1**: pigment with phase change materials (thermal comfort) and antibacterial capability.
- **PIGMENT 2**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and with anticorrosion capability.
- **PIGMENT 3**: pigment with phase change materials (thermal control) and self-cleaning capability to be incorporated in concrete for developing energy efficient building.
- **PIGMENT 4**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and antibacterial capability.

The new multifunctional NANOPIGMY pigments have provided their functionalities to the materials in which they are included with the final aim of improving sustainability of construction and automotive sectors at an efficient cost. They were dispersed into the materials for the development of final demonstrators, that is, in concrete, paints, and plastics. Six different materials have been developed by the dispersion of the four pigments developed during the project.

The properties of the final materials have been tested and the values have been compared with the values corresponding to the same materials, but with unmodified pigment and with the selected reference pigments. Finally, the materials have been validated by the final end-users of the project following the standards and norms required in construction and automotive sectors. The developed pigments fulfill with the REACH regulations, so a priori, no problems are expected for their commercialization. LCA and LCC analysis was carried out for the materials prepared with the multifunctional pigment.
4.1.2. Summary description of project context and objectives

NANOPIGMY project was born in a market immerse in a changing situation. The main driven forces for NANOPIGMY were:

**An automotive and construction markets with new needs**

The change in automobile and construction materials requirements has led industries to the modification of bulk materials with nanoparticulated additives or to the application of later high performance coatings in their materials to obtain better, cleaner, cheaper, faster and smarter products. However, there still exist some barriers to nanotechnology-based products commercialization and use:

- Manufacturing processes make the processes more complex
- High processing costs for nano-materials
- Need for qualified manpower

Modification of low-cost pigments could help to introduce nanomaterials (polymers, paints and concrete) in the market. Manufacturing processes in automotive and construction sector are commonly altered when nano-things are introduced in the materials formulation. With NANOPIGMY modifications, manufacturing processes would not be altered as the pigment gives itself the pursued functionalities and there would be no need of qualified manpower.

High performance pigments are pigments which offer a performance level which allows them to be used in wide variety of applications as they provide new or improved characteristics (pigments with an additional functionality apart from color). The high-performance pigment (HPP) market performed well in 2006 and continued to grow for a number of reasons but many of the raw materials used to manufacture HPPs increased in cost, thereby affecting the selling price of the finished goods to some extent. The price of high-performance pigments is significantly higher than classic pigments, and as a result, there are fewer producers of specialty pigments and higher margins for the products.

The use of modified low-cost pigment will help to reduce the price of HPPs and consequently the price of nano-materials.

*NANOPIGMY project seeks to produce cost-efficient multi-functional ceramic pigments with more functionalities than color to give to the automobile and construction materials (plastic, paint and concrete) the required functionalities through the use of these nanotechnology-based pigments, thus avoiding changes in manufacturing processes.*

**The growing position of China in ceramic pigments industry**

The impacts of the crisis are particularly visible in certain industries, such as the automobile industry and the construction sector which are changing their material requirements to adapt their businesses to the new environmental legislation and new consumer values 2,3. This

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2 “Responding to the Economic Crisis. Fostering Industrial Restructuring and Renewal” - OECD 2009
change in materials requirements (performance, environmental and cost requirements) generally involves the application of later functional coatings or the use of embedding nanoparticles, turning the material development process into a more complex process.

New materials requirements combined with the renewed emphasis placed on the joy of color are leading the pigment industry to the development of new types of pigments with more functionalities than color (e.g. thermal storage by embedding phase change materials, low emissivity, self-cleaning, anti-bacterial self-healing or anticorrosion) to give to the materials the required functionalities through the use of these pigments, avoiding thus later coatings (and involved problems as nano-additives agglomeration) and simplifying the materials ‘production processes.

Since the ceramic pigments industry started, it has provided stable revenues. Emerging markets like China and India continue to develop higher quality products, presenting a challenge to established HPP suppliers. Research and development in the European ceramic pigments industry is an evident need. Considering the lessening importance of Europe in world pigment production and world consumption and the continued growth in importance of China, India, Latin America, Middle East, Russia & CIS and Southeast Asia, there is a need in Europe of producing multifunctional and high performance innovative pigments at a low cost to capture this emerging market.

There is a need for the development in ceramic industry

The term “high performance pigment” is more usually met within the organic rather than inorganic literature. One of the problems with high performance inorganic pigments is the limitation in available chemistry, so that very few really new compounds have been developed in recent years. NANOPYGMY proposes the transformation of ceramic inorganic pigments into high performance pigments as the economic pressures of the last decade have dictated a main direction for product development: discovery and development of “new” and “improved” inorganic pigments with higher performing characteristics.

Gunter Buxbaum stated in “High Performance Pigments” that “A study of the “old fashioned” and almost forgotten workhorse pigment ultramarine blue could also be significant in the light of its revival through recently introduced new manufacturing technology. And so it is possible that, in the future, development of new manufacturing processes for “old” pigments and enhancement of their properties might well revitalize these products to the point where they could also join the ranks of truly high performance pigments” and this is the main objective of NANOPYGMY project.

Nanotechnologies capacity to transform ceramic pigments industry

Emerging nanotechnologies offer the potential to develop entirely new approaches for producing engineered active multi-functional pigments designed to reduce environmental and health impact in their final applications (construction and automobile industries) thus transforming a traditional industry like ceramic pigments industry into a new and competitive nanotechnology-based industry.

Ceramic pigments are inorganic compounds with high pigmentary properties. The most known inorganic pigment is Ultramarine blue whose manufacturing process was devised by Christian Gmelin in 1828. The ultramarine pigments are a family of mineral pigments characterized by the sodalite structure (which is the simplest zeolite and has the ability of

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3 “Nanoproducts in the European Construction Industry”, State of the Art 2009 - Executive Summary
trapping functional species) and colored species encapsulated inside. Apart from that, the ultramarine-based ceramic pigments’ price is very low compared to other HPP (up to 4€/kg).

Zeolite morphology of ceramic pigments joined with nanotechnologies, makes it possible to give to a pigment new functionalities apart from color. Multifunctionality of pigments will be achieved by different routes:
- Developing transparent and functional nanocoatings around the pigments surface by sol gel nanotechnology.
- By introducing functional nanoparticles or specific molecules (Phase Change Materials) on the sodalite surface.

By using these technologies ultramarine pigment, which is considered a cheap pigment, will be modified to obtain completely new multifunctional pigments.

Summarizing, the main objectives of NANOPIGMY project are:

**OBJECTIVE 1- Design and development (synthesis) of four multi-functional pigments at lab and pre-industrial scale**

The main objective of the project is the development of four multi-functional pigments by combining two technologies: 1. Sol-gel technology to obtain functional nanocoatings around pigments’ surface and 2. Embedding functional nanoparticles or active molecules on the pigment. The combination of functionalities targeted in the project are:

- **PIGMENT 1**: pigment with phase change materials (thermal comfort) and antibacterial capability.
- **PIGMENT 2**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and with anticorrosion capability.
- **PIGMENT 3**: pigment with phase change materials (thermal control) and self-cleaning capability to be incorporated in concrete for developing energy efficient building.
- **PIGMENT 4**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and antibacterial capability.

For the manufacturing of the pigments at pre-industrial scale, the pilot plant required for the preparation of each pigment has been designed and set up for the production of the 4 pigments.

**OBJECTIVE 2- Dispersion of developed multi-functional pigment in different matrix (paint, plastic and concrete)**

After defining the optimal quantity of pigments to be dispersed in different matrix, the dispersion of the four pigments will be done in paints, polymers and mortar. The next figure shows the matrix where each pigments will be dispersed. The main advantage of NANOPIGMY’s pigments is that conventional mixing techniques will be employed as the manufacturing processes is not altered by the presence of the new pigments.
OBJECTIVE 3 - Validation of developed materials

For the validation of the materials, their main properties have been tested by the consortium and they have been compared with the materials prepared with conventional unmodified pigments and with High Performance Pigments (HPPs).

For each pigment, requirements in terms of new functionalities were established (bactericidal ratio, thermal behavior, anticorrosion capability…). Besides, other specific properties oriented to the final use of the six materials prepared were established by the end-users in construction and automotive markets.

OBJECTIVE 4 - Validation of developed materials through prototypes

In order to demonstrate the benefits of developed materials with respect to materials currently present on the market, using as much real conditions as possible, two different demonstrators have been defined for the automotive sector and three for the construction sector. Each demonstration system has a reference component (with the unmodified pigment embedded) and a testing component (with the modified pigment embedded) to evaluate the improvements achieved with the developed multifunctional pigments.

For the prototypes related with the construction sector, shadow simulations were carried out using design Builder® and Sketch Up® software just before the construction phase so as to avoid undesirable shadowing effects among couple components, thus allowing mock-ups to receive the same averaged solar irradiance values (W/m²) during the day. The mock ups have been designed specifically for testing each material, selecting the construction materials to avoid thermal differences between the couple rooms.
A proper evaluation of the thermal performance, the bactericide behavior and the self-cleaning capability was carried out by using specifically designed tests.

For the prototypes of automotive sectors, an external part of a vehicle and a globe box cover have been prepared and validated following the FCA (FIAT Chrysler Automobiles) standards.

OTHER ISSUES TO BE TAKEN INTO ACCOUNT

To carry out the environmental monitoring, recycling cost analysis and safety/risks analysis of the introduction of the NANOPIGMY pigments-based materials in construction and automotive sectors.

- Evaluation of the environmental impact of conventional materials (with traditional pigments) in comparison to the new NANOPIGMY-based materials (Life Cycle analysis)

- Safety and risks analysis of conventional materials (with traditional pigments) in comparison to the new NANOPIGMY-based materials (Life Cycle analysis)

- Costs analysis of conventional materials (with traditional pigments) in comparison to the new NANOPIGMY-based materials (Life Cycle analysis)

- REACH standards will be used to handle the health and safety issues at using the nanopigments

Exploitation plan development (to build up a web site; to implement the dissemination plan and to develop an exploitation plan).
4.1.3. Main S&T results/foregrounds

DESIGN AND DEVELOPMENT (SYNTHESIS) OF FOUR MULTI-FUNCTIONAL PIGMENTS AT LAB AND PRE-INDUSTRIAL SCALE

The development of four different pigments has been achieved at lab and pre-industrial thanks to the strong collaboration between TEKNIKER and NUBIOLA, and the support in the characterization of AMU. As a summary, the functionalities of these pigments are:

- **PIGMENT 1**: pigment with phase change materials (thermal control) and antibacterial capability.
- **PIGMENT 2**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and with anticorrosion capability.
- **PIGMENT 3**: pigment with phase change materials (thermal control) and self-cleaning capability to be incorporated in concrete for developing energy efficient building.
- **PIGMENT 4**: pigment which could highly reflect the IR radiation for being used in energy efficient applications and antibacterial capability.

For the development of the pigments 1 and 3 at lab scale, a molecular modeling was carried out to study how the phase change materials (PCMs) to be introduced on pigment 1 and pigment 3 interact with pigments. The molecular modeling commercial suite Materials Studio 5.0 was used to conduct the study. All the simulations were performed using the COMPASS forcefield.

Initially, a sodalite surface was created from the initial supercell. 3D boundary conditions are applied to the computational cell leaving a 20 nm vacuum space between surfaces in the Z direction to simulate the pore size measured experimentally (Figure 1Top). A Monte Carlo (MC) simulation at T=298 K and P =1 atm was carried out to study the adsorption of a phase change material. The results show that molecules are adsorbed on the surface of the sodalite, location that is more favorable energetically than standing far from the surface (Figure 1, bottom).

![Figure 1. Top: Model of surface sodalite showing 4 computational cells. Bottom: configuration obtained after de MC run with the phase change material molecules adsorbed on the surface](image-url)
A Molecular Dynamics (MD) simulation was performed on the system obtained from the MC simulations in order to check if the adsorption on the surface is stable with time. After the simulation, no desorption of molecules was observed. On the contrary the layer phase change material evolves with time moving closer towards the surface (Figure 2).

![Figure 2. phase change material layer on the sodalite surface. Left: initial configuration before MD run. Right: Configuration after 10 ps of NVT MD simulation at room temperature](image)

Subsequently, the confinement between sodalite and SiO2 surfaces was also analyzed in order to study the interactions between the phase change material with the SiO2. For this purpose a layer of phase change material molecules was loaded between sodalite and SiO2 surfaces (Figure 3). After the loading step, a MD NVT simulation at room temperature was conducted for 10 ps with a time step of 1 fs. The simulation indicated the presence of attractive interaction energies between phase change material layer and sodalite and SiO2 surfaces.

![Figure 3. phase change material layer between sodalite and SiO2 surfaces. Top: initial state (before MD run). Bottom: final step after MD run](image)

Therefore, it can be possible to adsorb the PCM on the surface of the pigment and the PCM will remain on the surface due to attractive interactions. However, in order to avoid the future leakage of the PCM when the impregnated pigment was included in another material, it was decided to apply a coating around the impregnated pigment to encapsulate the PCM.

The formulation of the coating around the pigments was selected appropriately to provide the pigment with the new targeted properties, not affecting significantly the initial characteristics of the pigments, such as the acid resistance and color.
For the preparation of the pigments, firstly each functionality was studied independently and after obtaining a pigment with each individual functionality, the targeted combination of functionalities was applied simultaneously. Once the final composition of each pigment was completely defined at lab scale, the up-scaling of the procedures to obtain the pigments was checked in the preparation of an amount intermediate between few grams and kilograms. After solving some problems arisen in relation to the filtration of the pigments after their treatment, the process was implemented in NUBIOLA’s facilities.

For the manufacturing of the pigments at pre-industrial scale, the pilot plant required for the preparation of each pigment has been designed and set up for the production of the 4 pigments. The pigments obtained in the up-scaling presented similar properties than the pigments obtained at lab.

**DISPERSION OF DEVELOPED MULTI-FUNCTIONAL PIGMENT IN DIFFERENT MATRIX (PAINT, PLASTICS AND CONCRETE) AND VALIDATION OF DEVELOPED MATERIALS**

Multifunctional pigments have been further embedded in different matrices (plastics, cement and paints) with the aim of obtaining high-value added products avoiding posterior coatings, nanoparticles dispersion or surface modifications to give the product a specific needed functionality. Thus NANOPIGMY pigments development made it possible to obtain paint, concrete or a plastic with more than one functionality (apart from color) only through the use of these developed pigments. After defining the optimal quantity of pigments to be dispersed in different matrices, the dispersion of the four pigments was be done by the industrial partners. PIN and CHROMAFLO were in charge of the dispersion of the pigments in colorants and these colorants were further employed by the consortium for the preparation of functional paints. A paint with thermal control and antibacterial capabilities for interior applications was prepared and a paint for thermal control and anticorrosion was developed for being used in external paints in cars.

The procedure of preparing a colorant was described as well as the test procedure and the implementation in the paint. Figure shows the mill used to prepare the samples. Also this mill contains zirconia beads.

On the other hand, PMB was in charge of preparing a polypropylene (PP) masterbatch with thermal control and antibacterial capabilities for being used by the automotive industry. A high shear dispersion protocol was employed for the proper dispersion of the pigments. PP was mixed with the pigments and a pigment dispersant in a bag for a short period allowing the
liquid dispersant to coat the pigment and then adhere to the PP. The premix was introduced into the extruder TSA 15mm twin-screw to enable the screws to work under their optimal shear conditions. Downstream equipment cooled and pelletized the strands. The pelletized product from the extruder was flood fed into the injection moulder which operated on a standard cycle time for this type of molding. This masterbatch was further used by CRF for the preparation of a globe box frame with these properties.

In addition, thermoset polymeric materials with thermal control and antibacterial capabilities have been prepared for construction. The protocol for dispersing pigment 1 and 4 in an epoxy resin has been reported. A colorant was developed with the unmodified and modified pigment. Once the colorant was stable, systems epoxy/pigment were prepared and analyzed.

Finally, ACCIONA developed a mortar with self-cleaning and thermal control properties for being used in the outer parts of building. The dispersion process consists in the following steps: cement and water are mixed together in a mortar mixer and the mixture is stirred for 30s. The sand is added to the mixture and stirred for 30s. The mixture is paused for 90s and the material stuck in the walls is removed and incorporated to the bulk. During this settle time, pigments are added to the mixture and the mixture is stirred for 60s (Figure 6). The results showed that the procedure selected to incorporate the pigments in mortar matrix works well and homogeneous dispersion of the pigments is obtained. The dispersibility study of the pigment showed that pigment 3 is slightly better in dispersibility than the original non-modified pigment.

The final mixture is placed in a triple mold and compacted in an automatic mortar compacter (Figure 7). The Figure 7 showed also the mortar being molded in the molds.
The different materials have been validated at lab scale by the consortium and the results obtained for the materials prepared with the NANOPIGMY pigments were compared with the results obtained with the non-modified pigments and some high performance pigments (HPPs) commonly employed for the targeted functionalities in the construction and automotive sectors.

- **Material 1: Interior paint with pigment 1 for construction**
  A paint formulation with antibacterial and thermal storage behavior has been developed by the addition of pigment 1 without affecting negatively the adhesion and viscosity of the paint formulation. Regarding the thermal behavior of the paints, the paints with modified pigment 1 had better thermal efficiency than the paints with unmodified pigment. The antibacterial behavior of the paints prepared with the modified pigment is better than the one of paints with unmodified pigments.

- **Material 2: Polymer (epoxy) with pigment 1 for construction**
  The final material prepared with pigment 1 was an epoxy sandwich panel. The pigment was dispersed into the epoxy resin and then the system was mixed with the hardener. The epoxy/amine/pigment mixture was impregnated by hand into the fibres and allowed to cure under vacuum for 24 hours. Then both sheets of laminate were glued to the core (see Figure 8).
The viscosity of the epoxy modified with pigment 1 was not increased significantly with the addition of the modified pigment and it allowed working properly with the modified resin. Regarding the thermal behavior, the epoxy/amine system with modified pigment 1 had better thermal efficiency than the epoxy with unmodified pigment. In relation with the antibacterial activity, the polymeric sandwich panel used for the demonstrator presented better bactericide results than the panels prepared with the unmodified pigment. The addition of the pigment into the epoxy matrix did not affect negatively the mechanical properties of the sandwich panel.

Summarizing, pigment 1 can provide antibacterial and thermal storage behavior without affecting negatively the viscosity of the resin and the mechanical properties of the panel, but an increased amount of epoxy/hardener/pigment should be incorporated in the final composites (increasing the number of layers of glass fibre for example).

- **Material 3: Paint with pigment 2 for automotive application**

The formulation with modified pigment 2 improved the anticorrosive performance of the formulation made with the unmodified pigment (comparing the results after 1500 h in the corrosion chamber) and presented an improvement in TSR, apart from giving color. In addition, the paint prepared with pigment 2 presented similar adhesion to the substrate than the pristine paint, so the pigment does not affect negatively the adhesion.

To validate the anticorrosion properties of the developed pigments, a paint has been prepared by dispersing the modified pigment in a formulation employed in the automotive sector. The results have been compared with the one corresponding to paints prepared with the anticorrosion pigments conventionally employed in the market (Nubirox 106 and Nubirox 302) and with the paints prepared with the unmodified pigment. In Figure 9 is shown the final appearance of the substrates after 1500 h in the corrosion chamber (ASTM B117).
Main results concerning the anticorrosion behavior are also collected in Table 1. The adhesion of the paint to the substrates is good in all the systems. Comparing in the substrates the width of the incision made on the coating and the rusting, it seems that formulation with modified pigment 2 improved the anticorrosive performance of the formulation made with the unmodified pigment and also some values obtained for the formulations with the HPPs.

Table 1. Anticorrosion properties of the studied paint formulations after 1500 h in the corrosion chamber

<table>
<thead>
<tr>
<th></th>
<th>PIGMENT 2</th>
<th>UNMOD. PIGMENT</th>
<th>HPP1</th>
<th>HPP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>RUSTING AT THE SCRIBE</td>
<td>mm rusting at the scribe</td>
<td>2.0</td>
<td>3.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Classification ATM D</td>
<td>1654-91 (A)</td>
<td>7</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>RUSTING ON THE SUBSTRATE</td>
<td>Rusting classification ASTM D 610-68</td>
<td>none</td>
<td>none</td>
<td>8G</td>
</tr>
<tr>
<td>% rusted area</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>Classification ASTM D610-68</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Oxidation value</td>
<td>9</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

- **Material 4: Mortar with pigment 3 for construction**
  A mortar formulation with self-cleaning and thermal storage behavior has been developed by dispersing an optimized content of pigment 3. Regarding the thermal behaviour of the mortar, the increase of the pigment content in the mixture leads to the increase in the thermal efficiency of the material.
  Concerning the self-cleaning property, the criteria followed in construction applications to determine if a material is self-cleaning or not is to achieve an index of photocatalytic activity (IAF) > 0.1 in 8 hours. This criterion has been adopted in the project. The IAF variation with time of the mortar greatly increases during the test. Therefore, the self-cleaning behavior is clearly shown in Figure 10.

In addition, adding the unmodified and modified pigment into the mortar didn’t alter the consistence and the mechanical properties of the mortar. Besides, the flow values of these systems are very close to a reference mortar without pigment.

- **Material 5: Polymer with pigment 4 for automotive sector**
A new multifunctional pigment 4 with IR high reflective capabilities and antibacterial properties was included in polypropylene (PP) by extrusion and injection molding. PP composites with modified pigment 4 improved antibacterial results when compared with PP mixed with unmodified pigment. In addition, the final PP material presented an improved TSR value when compared with the HPP and with the unmodified pigment.

- **Material 6: Polymer with pigment 4 for construction**
A new multifunctional pigment 4 with IR high reflective capabilities and antibacterial properties was included in the epoxy resin by a dissolver dispermat Cowles. The epoxy/pigment mixture was mixed with the hardener (amine) to prepare the final system with the pigment. The epoxy/amine/pigment mixture was impregnated by hand into the fibres for preparing the composites (see Figure 8). The addition of the pigment in the epoxy matrix doesn’t affect the mechanical properties of composite material. They have similar tensile properties values as the pure composite panel. Concerning the antibacterial properties, the material with the modified pigment showed a 99.3 - 99.95 % reduction of Colony forming units, expressed as comparison with control.

**VALIDATION OF DEVELOPED MATERIALS THROUGH PROTOTYPES**

In order to demonstrate the benefits of developed materials with respect to materials currently present on the market, using as much real conditions as possible, two different demonstrators have been defined for the automotive sector and three for the construction sector. Each demonstration system has a reference component (with the un-modified pigment embedded) and a testing component (with the modified pigment embedded) to evaluate the improvements achieved with the developed multifunctional pigments.

**VALIDATION OF THE CONSTRUCTION MATERIALS**

For the prototypes related with the construction sector (prototype 1, 2 and 3), shadow simulations (see Figure 11) were carried out using design Builder® and Sketch Up® software just before the construction phase so as to avoid undesirable shadowing effects among couple components, thus allowing mock-ups to receive the same averaged solar irradiance values (W/m2) during the day.

![Figure 11. Example of shadow simulation using Design Builder and Sketch Up Software](image)

Once decided the position of the demonstrators, different mock ups were designed and built for testing each material. The main characteristics of the employed mock ups and the results of the validation tests were described below:
Prototype 1-Material 1: Interior paints with antibacterial and thermal storage capabilities for construction applications (inclusion of PIGMENT 1 in interior paints formulations).

Mock-ups used to house Material 1 were decided to be lightweight to allow appreciate possible thermal differences between the couple rooms (see Figure 12), due to the low energy storage capacity and poor amount of PCM present in the paint composition.

The mock-ups count on one door on the Northern façade, one window on the Eastern one, and one additional window on the Western wall. After some simulations, Southern window was blocked with a commercial insulation system (XPS panel, \(\lambda=0.034\) W/mK) in order to avoid excessive solar gains throughout the glasses.

For a proper evaluation of the thermal performance of the materials in the prototypes, a sensor distribution has been designed and optimized taking into account the channels in the data logger and temperatures or conditions the NANOPIGMY consortium was interested to follow-up.

For the monitoring of the bactericide behaviour, a high humidity testing bathroom with an effective surface of 20 m² has been prepared. Bathrooms are areas of high risk for the growth of micro-organisms which have a negative influence on indoor air climate and can cause all kinds of health problems. The range of temperatures and relative humidity levels typically present in bathrooms favors the growth of fungi. Furthermore, the three types of basic
finishing materials studied in this project (paints, plasters and ceramic tiles) are encountered side-by-side in bathrooms, making the bathroom a very fine and practical research example. A programmer of automatic irrigation was installed in the shower. The temperature and relative humidity conditions inside the bathroom have been regularly monitored.

For the validation of the material 1 in prototype 1, the interior paint with antibacterial and thermal storage capabilities for construction applications has been applied in the inner part of the mock-ups. Before materials installation, thermal differences between paired mock-ups during the thermal test carried out were found to be lower than 0.5°C, which corresponds to the typical accuracy rates of a T-Type thermocouple. The internal temperatures have been plotted, looking for a clear trace of the energy storage capacity and the active thermal insulation effect theoretically provided by the PCMs.

In Figure 13 is depicted Material 1 test-cells internal temperature for the whole testing period in the free-floating regime (from Jul 25th to Oct 28th). As it can be seen, taking into account PCM Melting Point (21°C), the optimal period for a zoom-in analysis is focused on interval starting from Sept 17th to Oct 4th. Within this interval, thermal waves oscillate around Melting Point (Tm±ΔT), naturally allowing charge and discharge process necessary for a PCM proper activity. In the chosen period, the thermal waves show no delays due to PCM thermal activity, having both waves exactly the same frequency during the testing period. Peak-to-peak differences during maximum irradiance hours are lower than sensor accuracy (±0.5°C).

Concerning the U-values, focusing on Western wall, figures show very similar values for the insulation coefficient, and it is considered to be near 10.0 W/m²K ± 1 W/m²K for Reference case and 11.1 W/m²K ± 1 W/m²K for NANOPIGMY case. Thus, both can be considered similar regarding method accuracy and expected error. Time interval for the whole test period was 14 days, which is more than the minimum required by the literature.

Material 1 energy consumption test was carried out for 14 days. Daily energy consumptions show very similar values, being the cumulative energy consumption for the whole testing period 90.2 kWh for NANOPIGMY test-cell and 92.9 kWh for the Reference case. Thus, NANOPIGMY energy consumption output was 2.9% lower than Reference one for the developed test.
On the other hand, the bactericide study started in July 2014 and finished in February 2015. The information gathered by the sensors located in the different positions on the walls and ceiling showed no significant variance in temperature and R.H. The temperature conditions and R.H. were inside the optimal range for the microorganism proliferation throughout the demonstration study. After the application of a suitable shower program, the material was exposed to triggering growth conditions throughout the whole period of evaluation of the bactericide performance. Bacterial and fungal spores were inoculated on the surface of the materials. The presence of spores made feasible a faster evaluation of the effectiveness of the materials containing the NANOPIGMY pigments to kill microorganism with respect to the effectiveness of the standard equivalent non-biocide products. In this framework, the purpose of the inoculation is to accelerate the progress of the demonstration by subjecting the materials to triggering conditions. Thus, the biocide behaviour of the NANOPIGMY materials can be tested in shorter times.

For the antimicrobial performance evaluation two approaches were followed:
- Visual testing every week to watch over fungal growth.
- Biological testing every 2 months to count the bacteria colony, which cannot be assessed by visual methods.

The results observed were highly dependent on the painted area. The evolution of microorganism growth on the walls protected by the Material 1, which contains the reference and the NANOPIGMY pigments, is the following. After one month of demonstration, first fungal growths surfaced on the reference and the NANOPIGMY walls. Nonetheless, the percentage of surface area covered by mold was significantly higher on the reference wall than on the NANOPIGMY wall. This fact indicates that the NANOPIGMY paint showed higher resistance to first mold emerging than the reference one. After three months of exposition, the fungal growths detected during the first month continued growing at a considerably high rate. The area covered by mold in the reference and the NANOPIGMY walls was comparable. From month three to month five, the above-referred mold stains continued expanding but at a much lower growth rate than from month one to month three of demonstration. The area covered by mold in the reference and the NANOPIGMY walls was comparable. From month five to month eight, growth of existing fungal species continued at a quiet rate. After eight months of demonstration, the coverage on the reference wall (around 60%) is slightly higher than on the NANOPIGMY wall (around 50%), but this minute difference could be considered negligible.

The evolution of microorganism growth on the roof protected by the Material 1, which contains the reference and the NANOPIGMY pigments, is described in Figure 14.

![Figure 14. Evolution with time of the aspect of the roof during the test](image)

After one month of demonstration, the first mold stain emerged on the reference material, whereas the NANOPIGMY material remained fully protected against mold. This is evidence of the higher resistance to biological growth of the NANOPIGMY material. After two months
of demonstration, a number of fungal growths could be observed on the surface of the reference paint, whilst only a little fungal stain covering less than 1% of the material’s surface was exhibited by the NANOPIGMY material. After five months of demonstration the growths on the reference material continued growing at a considerably high rate, whereas the NANOPIGMY paint showed almost full resistance to new growths and prevent the existing mold stains on its surface from continuing growing. At the end of the testing period the better biocide performance of the NANOPIGMY paint was consistently proven. Whilst the part of the roof painted with the reference formulation had been visibly affected by fungal attack and around 25% of its area had been covered by mold, the part painted with the NANOPIGMY formulation barely showed fungal presence.

Concerning the biological test results, when material 1 is applied on the wall, the NANOPIGMY formulation did not show enhanced biocide behaviour than the reference one. The results of the biocide test performed after two weeks of application of showers indicated that both formulations, NANOPIGMY and reference, had been able to kill all the bacteria present in the environment. However, as the demonstration progressed in time, both formulations of Material 1 lost their capacity to kill the bacteria attacking the materials, and therefore, the biological test carried out after three, six and eight months of demonstration found that there was high concentration of bacteria on the surface of the NANOPIGMY and reference paints installed on the wall. When material 1 is applied on the roof, the NANOPIGMY formulation did demonstrate significant better bactericide performance than the reference one. However, the bacteria removal action of Material 1 decreased as the time progressed. The two first tests, carried out after two weeks and after three months from the beginning of the showers respectively, indicated that both formulations, NANOPIGMY and reference, were able to kill all the bacteria present in the environment. However, the reference formulation lost its biocide activity partially after six months and totally at the end of the demonstration whereas the NANOPIGMY formulation has proven to be capable to resist bacterial attack totally until month six and partially until the end of demonstration. Figure 15 shows the results of the four biological tests performed throughout the testing period in terms of number of colonies grown on the NANOPIGMY’s and the reference’s samples.

![Figure 15. Number of colonies grown on NANOPIGMY’s and Reference’s samples taken from Material 1 applied on the roof of the demonstration set-up](image)

In Figure 16, it is possible to see the results obtained in the biological test for the material 1 and the reference applied on the roof after 8 month of the demonstration activity. The number of bacteria growth in the Petri dish corresponding to the bacteria in contact with material 1 is significantly lower than in the case of the reference material.
Prototype 2-Material 2: Sandwich panels with antibacterial and thermal storage capabilities for construction application (inclusion of PIGMENT 1 in epoxy resins).

The polymer sandwich panels (Material 2) where mechanically fixed to a lightweight brick masonry to serve as a structural guide for the panels stability in order to prevent the collapsing down of the polymer skin of the inside walls after installation process (see Figure 17).

The mock-ups count on one door on the Northern façade, one window on the Eastern one, and one additional window on the Western wall. After some simulations, Southern window was blocked with a commercial insulation system (XPS panel, $\lambda=0.034$ W/mK) in order to avoid excessive solar gains throughout the glasses.
For the evaluation of the materials in the prototypes, the following sensor distribution has been employed.

For the monitoring of the bactericide behaviour, the same device as for prototype 1 was employed.

For the validation of the material 2 in prototype 2, as in the previous prototype, the test cell structure has been validated before materials installation. Material 2 test-cells internal temperature for the whole testing period in the free-floating regime (Jul 25th to Sep 28th) is shown in Figure 18. Taking into account PCM Melting Point (23°C), the optimal period for a zoom-in analysis is focused on interval starting on Sept 12th and finishing on Sep 24th. Within this gap, thermal waves oscillate around Melting Point $T_m \pm \Delta T$, allowing the charge and discharge of PCM. For the optimal period. Neither time delays due to the presence of an active component with energy storage capacity nor changes in second derivative near Melting Point are observed, which suggest PCM thermal activity does not affect comfort temperature in any measurable way.

Concerning the U-values, figures show very similar values for the insulation coefficient both for the Western wall (1.75 W/m2K ± 0.18 W/m2K for Reference case and 1.75 W/m2K ±
0.18 W/m²K for NANOPIGMY case) and the Southern one (1.75 W/m²K ± 0.18 W/m²K for Reference case and 1.43 W/m²K ± 0.14 W/m²K for NANOPIGMY case). Thus, U-values can be considered to be equivalent for both test-cells regarding standard method accuracy and experimental expected error. Time interval for the whole test period was 12 days, which is more than the minimum required by the literature.

The Material 2 energy consumption test was carried out during 14 days. Daily energy consumptions show a clear tendency, being Reference energy consumption 0.5 kWh/day higher than NANOPIGMY case in all the studied data. Cumulative energy consumption for the whole testing period was 62.9 kWh for NANOPIGMY and 70.0 kWh for the Reference case. Thus, NANOPIGMY energy consumption output was 7.4% lower in average than Reference case.

On the other hand, the bactericide study started in July 2014 and finished in February 2015. During the antimicrobial performance evaluation, by using the visual testing every week to watch over fungal growth, no growth was seen on the Material 2 within the eight months of testing, (nor on the reference neither on the NANOPIGMY sandwich panels). Therefore, any conclusion with regard to the biocide behaviour of the Material 2 can be stated based on visual evaluation (Figure 19).

![Figure 19. Evolution with time of the aspect of the walls during the test](image)

Concerning the biological test results, biological tests indicated that the NANOPIGMY formulation had a similar good bactericide performance than the reference one. In this case, the hydrophobic surface of both panels could contribute to the good performance, avoiding taking proper conclusions of the efficiency of the NANOPIGMY’s pigment 1.

**Prototype 3-Material 4:** Exterior concrete with energy storage application and self-cleaning behavior (inclusion of PIGMENT 3 in a mortar render top coat on a brick facade).
Mock-ups coated with mortar render top coat (Material 4) where decided to be built in brick since mortar is normally applied on this kind of surface.
Material 4 mock-ups count on one door on the Northern façade and one window on the Eastern one. After some simulations, Southern window was blocked with a commercial insulation system (XPS panel, $\lambda=0.034$ W/mK) in order to avoid excessive solar gains throughout the glasses.

For the monitoring and evaluation of the materials, a sensor distribution has been designed and optimized for prototype 3.

The monitoring of the self-cleaning capability was carried out by following:

- Colour changes tracking to evaluate the soiling degree.
- Rhodamine B discoloration to evaluate the self-cleaning, repeated each three months.

In both cases the color changes are being monitored with a colorimeter. The results from the colorimeter are expressed in the CIELAB with $L^*$, $a^*$ and $b^*$ colourimetric coordinates.
For the validation of the material 4 in prototype 3, as in the previous prototypes, the test cell structure has been validated before materials installation. Material 4 test-cells internal temperature for the whole testing period in the free-floating regime (Jul 25th to Oct 28th) is shown in Figure 21.

As it can be seen, regarding PCM Melting Point (21°C), the optimal period for a zoom-in analysis is focused on interval starting in Sept 28th and ending up in Oct 8th. During this time gap, thermal waves oscillate around Melting Point $T_m \pm \Delta T$, allowing the charge and discharge process of the PCM substance. For the optimal period, neither time delays due to the presence of an active component with energy storage capacity nor changes in second derivative near Melting Point can be appreciated, which suggest building envelope is too thick to allow PCM heat transfer contribution to beat thermal resistance of the full building envelope, revealing its effect in the room temperature.

In Figure 22 are represented plots temperature registered by thermocouple placed between the mortar layer and the brick surface versus time for the representative period. This thermocouple is protected by a few millimeters of mortar and is the one capable to track the PCM effect in case it is measurable (>0.5°C between the mortar-brick interface). As it can be seen, Reference mock up show higher temperature values for temperatures above 35-40°C. Below 35-40°C, thermal behaviour is exactly the same for both thermocouples. If it is represented the thermal information from the same pair of thermocouples during part of the same period, some effects are appreciable for temperatures higher than 35°C, when Reference values get away.
Concerning the U-values, figures showed very similar values for the insulation coefficient both for the Western wall (0.33 W/m²K ± 0.03 W/m²K for Reference case and 0.40 W/m²K ± 0.04 W/m²K for NANOPIGMY case) and the Southern one (0.33 W/m²K ± 0.03 W/m²K for Reference case and 0.33 W/m²K ± 0.03 W/m²K for NANOPIGMY case). Thus, U-values can be considered to be similar for both test-cells regarding method accuracy and expected error.

Material 4 energy consumption test was not carried out since Material 4 faces the exterior. PCM charge and discharge process is only possible by means of heat transfer coming from an external source, being impossible to control weather conditions in a real scenario.

Concerning the self-cleaning performance of the material, as explained previously, two different strategies have been followed to evaluate the self-cleaning performance of Material 4:
- Color change tracking to evaluate the soiling degree
- Rhodamine B degradation to evaluate self-cleaning performance

In the color change tracking, colorimetric measurements were taken since the beginning of the demonstration until the end of the NANOPIGMY project, therefore from July 2014 to February 2015. This testing period covers 243 days. Changes in b*, L* coordinates are less for NANOPIGMY than Reference as can be seen from the figures.
The Rhodamine degradation tests have been performed since the beginning of the demonstration. The first test was carried out on the 1st of July 2014. The second test was done on the 20th of October 2014. And the last test was performed on the 2nd of February 2015. The values for the index of photocatalytic activity were higher than 0.1 for at least 1 wall in each of the three Rhodamine experiments. This means that NANOPIGMY Material 4 has self-cleaning capability.

It should be remarkable that the results obtained for the three tests are consistent with the solar radiation intensity change experimented by each façade during the year. The percentage of solar radiation in summer is greater for the East and West facades, while in winter time the percentage of solar radiation is greater for the South facade.

**Life Cycle Analysis (LCA) analysis for the construction industry**
For the LCA of developed materials in the **construction industry**, the basis of the study, i.e. functional unit, is: “Environmental impact of a building over 100 year period”.

The starting point considered in this study is the building envelope and equipment installed within it. This covers the building structure including walls, windows, roof and also the building systems for heating and cooling. The second point considered is the building operation and maintenance. This includes energy required to heat and cool the building as well as the cleaning regime. A typical office building located in Spain has been considered in this analysis and it has been subdivided into 2 Base cases and 4 Alternatives (More information can be found in D7.1 and D7.2).

![Model of the building](image)

Model of the building consists of five office spaces, one corridor and toilet facilities. Total footprint area is 519m2 and the layout and function areas of the model remain the same across the whole study

The main conclusions of this study are the following.

- For all Alternative scenarios the cradle-to-grave (embodied) environmental impact was found to be higher than for the relevant Base Cases. This is due to the use of additional materials in production of NANOPIGMY pigments in comparison to HC-42H and Nubicem.
- The cradle-to-grave life cycle assessment of all scenarios using the ReCiPe methodology shows that the total environmental impact of Alternative buildings is between 3.5kPt and 20kPt lower than the Base Case buildings. The average reduction is 10kPt, which is equivalent to ten average persons’ annual environmental load. This is due to the reduced quantity of cleaning materials and reduced energy used for the heating and cooling the building.
- For the whole life cycle assessment, manufacture of building elements and their maintenance accounts for between 15% and 20% of the total environmental impacts. The average is 17%. This is attributed to high energy consumption, for cooling and heating, during building operation stage. The end of life stage, where building waste is accounted for, represents only 1% of the total impact of the building.
- According to IPCC (2013) impact assessment, NANOPIGMY offices’ lifetime GHGs emissions are lower than those of the reference buildings.
• The majority of overall life cycle GHGs emissions (CO$_2$-equivalent) are associated with operational emissions from cooling and heating the building (between 78% and 82%). The cradle-to-grave GHGs (embodied carbon dioxide emissions) associated with the materials using NANOPIGMY pigments are higher than traditional materials because of the additional materials, such as ethanol, rubitherm PCM, used to produce the NANOPIGMY pigments.

• The Alternative buildings’ average embodied carbon emissions, i.e. cradle to grave, were found to be between 0.2% and 0.5% for the different alternatives. The same buildings’ average life CO$_2$ emissions, i.e. cradle to grave, were found to be between 15% and 4.9% lower comparing to reference buildings.

**Life Cycle Cost (LCC) analysis for the construction industry**

The life cycle cost calculations show that with the use of the modified paint and the render using NANOPIGMY pigment, there are obtained economic benefits in net present value terms over a 100-year period at a discount rate of 6%. A typical office building has been considered for the product systems to be analysed.

The life cycle cost calculations show that with an interior paint incorporating NANOPIGMY pigment 1, providing antibacterial and thermal storage properties which is planned to reduce the costs of internal cleaning and heating/cooling the building, with an external render incorporating NANOPIGMY pigment 3, providing self-cleaning and thermal storage properties which is planned to reduce the costs of external cleaning and heating/cooling the building and which uses an interior paint incorporating NANOPIGMY pigment 1, providing antibacterial and thermal storage properties, and external render incorporating NANOPIGMY pigment 3, providing self-cleaning and thermal storage properties, deliver economic benefits in net present value terms over a 100-year period at a discount rate of 6%. In these cases, the additional cost of the NANOPIGMY pigment is more than offset by reductions in energy consumption and in maintenance costs. It is likely that these benefits will also be seen under different circumstances, such as shorter study periods or different discount rates, but none of these sensitivity analyses have been carried out.

However, using NANOPIGMY polymer board with pigment 1 (providing antibacterial and thermal storage properties which is planned to reduce the costs of internal cleaning and heating/cooling the building) has a higher life cycle cost over 100 years at a 6% discount rate. Here, the additional cost of the NANOPIGMY pigment is substantial and is not offset by reductions in energy consumption and cleaning costs. In these cases, the additional cost of the NANOPIGMY pigment 1 is more than offset by reductions in energy consumption and in maintenance costs. It is likely that these benefits will also be seen under different circumstances, such as shorter study periods or different discount rates.

VALIDATION OF THE AUTOMOTIVE Materials

For the validation of the materials in the automotive sector, two different demonstrators have been defined.

**Prototype 4-Material 3: Exterior paints with anticorrosive and low emissivity capabilities for automotive application (inclusion of PIGMENT 2 in exterior paint formulations).**

For **Prototype 4** (Exterior paints with anticorrosive and low emissivity capabilities) testing, standard substrates composed by steel + phosphate coats + e-coat have been coated by spraying.
To develop real application for demonstrators, a part of car/vehicle’s body, currently in production, has been determined for further paint. Due to size and weight issue the mudguard of FIAT New Ducato 2014 has been selected. Following pictures (Figure 25) report the mudguards with e-coat and paint-coated.

Figure 25. FIAT New Ducato 2014 mudguard: e-coat part (left) and painted part (right)

As described the automotive painting system (excluding the e-coat) is composed by 3 layers at least: Primer-Basecoat-Topcoat (see Figure 26). However NANOPIGMY target is on single/double layer systems as today used especially for industrial vehicle as well as trucks. Scheme of targeted system is following reported. Multisystem plaques and substrates composed by: Steel-plaques + phosphate coats + e-coat are suitable for adhesion reason. The formulation components and processing parameters currently employed at CRF have been maintained.

Figure 26. The target system as proposed in NANOPIGMY

The introduction of the automobile mass production line, in combination with the development of new synthetic paint technology, was the major factor in the adoption of spray application. A common method to improve spray efficiency is to use automatic machines with some ‘hand reinforcing’ in difficult recessed areas and interiors. It has the added advantage of reducing labour. NANOPIGMY demonstrators are produced by automatic process in plant as e-coat coating in batch methods and manually by spray paint application.

The characterization of final demonstrators as well as preliminary plaques has been carried out following the FCA (FIAT Chrysler Automobiles) standards. These standards have been harmonized during the 2014 and define all the validation procedure in terms of process application and materials resistance. Consequently, CRF applied to the NANOPIGMY demonstrators all the expected tests following the logical development phase. Table 2 collected all the expected tests.

Table 2. Expected DOE for NANOPIGMY samples: painted components

<table>
<thead>
<tr>
<th>TEST</th>
<th>STANDARD</th>
<th>DESCRIPTION</th>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual Inspection</td>
<td>ASTM_D0523</td>
<td>L, a*,b* R spectra</td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>SSQ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesion</td>
<td>ASTMD3359</td>
<td>Cross cut test</td>
<td></td>
</tr>
<tr>
<td>RESISTANCE TO</td>
<td>FGA-50473</td>
<td>Gasoline at RT for</td>
<td></td>
</tr>
</tbody>
</table>
GASOLINE | 1hr | 60°C for 24hrs | FGA-50470 |
---|---|---|---|
Resistance to water immersion | FGA-50184 | 150hr @40°C with RH95-100% |
Resistance to humidity | FGA-50180 | B2 → 100hrs C2 → 300hrs |
Resistance to corrosion SST | FGA-50461 | Aging in wheatermeter with Xenon 750hrs |
Accelerated ageing under atm agents | FGA-50488/01 | After stone chipping test sat spray 24hrs |
Resistance to stone blow | FGA-50488/01 | 10washing cycles |
Scratching test by car-wash | FGA-50488 | Only for production component (100hr at development stage) |
Scratching test by car-wash | FGA-50449 | Only for production component (mar test at development stage) |

The evaluation procedure follows the procurement specification FIAT 955842 named VARIOUS METALLIC PARTs. Within the standard a general division of main classes of car surfaces are described. So the CLASS B2 parts are surfaces in direct contact with the atmospheric agents and the sunlight while the CLASS C2 ones are exposed parts, based on the position on the vehicle, to corrosion and to sunlight. The surfaces as defined in NANOPIGMY are CLASS B2.

Finally a custom test to evaluate the capability of IR shield has been carried out. The painted plaques have been evaluated by total %R in the range VIS-NIR (300-2500 nm). The capability to reflect the wavelengths in NIR region confirm the capability to reflect the heat from the environment. Further tests are currently under evaluation as the exposure of component to heat source and the evaluation of local temperature through a set of thermocouples. However the complexity of the multi-layered systems does not allow the evaluation of the contribution of single component.

A Summary of performed tests is reported in Table 3. In order to improve the coverability of the paint selected for the study TiO₂ has been added to the paint. This is a conventional additive in the industry of paints for automotive sector. The results obtained for the paint prepared with the unmodified and modified pigments were positive, but not significant differences have been obtained for the paints prepared with the multifunctional pigment.

Table 3. Main characterization results obtained by CRF
The resistance to corrosion test, carried out in accordance with the standard FGA-50180, has been carried out considering exposures periods much lower than the exposure times used in the analysis of the materials at lab scale. The differences at lab scale appeared for longer exposure times. However, it worth to mention that fir longer times, more significant differences have been checked at lab scale.

Concerning the capability of IR shield of the painted plaques, it has been evaluated by total %R in the range VIS-NIR (300-2500 nm). An integrating sphere was to get all the reflected light in the space. The light scattered by the interior of the integrating sphere is evenly distributed over all angles. The capability to reflect the wavelengths in NIR region confirms the capability to reflect the heat from the environment. An enhancement of 8.6% of reflectance within all the NIR range (750-2300 nm) was observed (see Figure 27).

![Figure 27. Total Reflectance spectra (200-2300 nm)](image)

**Prototype 5-Material 5:** An interior polymeric component of a car. Specifically, a globe box frame for the car made of polypropylene. (Inclusion of PIGMENT 4 in polypropylene).

The development of specific pigments will be useful for several applications in interiors as cover frames of dashboard.
The pigments employed in this application have been previously mixed with standard polypropylene by PMB in an extruder. Then the manufacturing of components needed the mix of pigments masterbatch and the base raw material (polypropylene for automotive applications). The mix has been carried out by mixing tool at selected temperature and quantity. PIOVAN mixer tool has been used together with Sandretto 330tons IM tool (see Figure 29).

In Figure 30 the demonstrators of PP raw material (White) and the demonstrator with different amount of NANOPIGMY’s masterbatch are shown.
The characterization of final demonstrators as well as preliminary plaques has been carried out following the FCA (FIAT Chrysler Automobiles) standards. These standards have been harmonized during the 2014 defining all the validation procedure in terms of process application and materials resistance. Consequently, CRF applied to the NANOPIGMY demonstrators all the expected tests following the logical development phase. Table 4 collects all the expected tests.

<table>
<thead>
<tr>
<th>TEST</th>
<th>STANDARD</th>
<th>DESCRIPTION</th>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidity of new materials</td>
<td>ISO1133</td>
<td>Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics.</td>
<td>Very important to realize the final demonstrator. In that case the value should be around 36-44 g/10 min</td>
</tr>
<tr>
<td>Visual Inspection</td>
<td>FIAT Standard</td>
<td>Evaluation of colour of aesthetical surfaces L, a*, b* R spectra</td>
<td></td>
</tr>
<tr>
<td>Antiscratch</td>
<td>FIAT Standard</td>
<td>Scratch and mar resistance of automotive plastics using Erichsen scratch hardness tester</td>
<td></td>
</tr>
<tr>
<td>Tensile test</td>
<td>ISO527</td>
<td>UTS and Elongation</td>
<td></td>
</tr>
<tr>
<td>Flexural test</td>
<td>ISO178</td>
<td>Elastic modulus</td>
<td></td>
</tr>
<tr>
<td>IZOD Impact</td>
<td>FIAT Standard</td>
<td>Resilience</td>
<td></td>
</tr>
<tr>
<td>VICAT</td>
<td>FIAT Standard</td>
<td>Softening temperatures</td>
<td></td>
</tr>
<tr>
<td>High Temperature Distorsion HTD</td>
<td>ISO75 - (load = 1.8 MPa)</td>
<td>Distortion at high temperatures</td>
<td></td>
</tr>
<tr>
<td>Accelerated ageing under atm agents</td>
<td>FIAT Standard</td>
<td>Fade-meter. T 60°C, RH 55%, Continuous exposure</td>
<td>Time: * 75 h: Parts which are not directly exposed * 150h: Indirectly exposed parts * 300h: Directly exposed parts</td>
</tr>
</tbody>
</table>

The evaluation procedure follows the procurement specification 9.55253 for interior plastics, already harmonized between FIAT and Chrysler.

The new materials developed with the multifunctional pigments have been validated at conditions close to real conditions. Prototype 5 has been prepared by mixing the masterbatch samples with 40 wt% of modified and unmodified pigments prepared by PMB with the base raw material (polypropylene for automotive applications). The characterization of final demonstrators as well as preliminary plaques has been carried out following the FCA (FIAT Chrysler Automobiles) standards. The evaluation procedure follows the procurement specification 9.55253 for interior plastics, already harmonized between FIAT and Chrysler. In order to demonstrate bacterial and thermal benefits of NANOPIGMY’s prototype 4, it has been decided to analyze the material in the shape of plane plaques in order to avoid the...
influence of the geometry of the final piece in the results. A Summary of performed tests is reported in Table 5.

Table 5. Main characterization results obtained by CRF

<table>
<thead>
<tr>
<th>Focus</th>
<th>Test</th>
<th>Standard</th>
<th>Description</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Fluidity of new materials</td>
<td>ISO1133</td>
<td>Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics.</td>
<td>OK</td>
</tr>
<tr>
<td>Aesthetic</td>
<td>Visual Inspection</td>
<td>FIAT Standard</td>
<td>Evaluation of colour of aesthetical surfaces L, a*,b* R spectra</td>
<td>OK</td>
</tr>
<tr>
<td>Reliability and resistance</td>
<td>Antiscratch</td>
<td>FIAT Standard</td>
<td>Scratch and mar resistance of automotive plastics using Erichsen scratch hardness</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>Tensile test</td>
<td>ISO527</td>
<td>UTS and Elongation</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>Flexural test</td>
<td>ISO178</td>
<td>Elastic modulus</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>IZOD Impact</td>
<td>FIAT Standard</td>
<td>Resilience</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>VICAT</td>
<td>FIAT Standard</td>
<td>Softening temperatures</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>HDT</td>
<td>ISO75 - (load = 1,8 MPa)</td>
<td>Distortion at high temperatures</td>
<td>OK</td>
</tr>
<tr>
<td></td>
<td>Accelerated ageing under atm agents</td>
<td>FIAT Standard</td>
<td>Fade-ometer. T 60°C, RH 55%, Continuous exposure</td>
<td>OK (75hr and 150 hr more robust than unmodified)</td>
</tr>
</tbody>
</table>

The results concerning the antibacterial properties against E. Coli showed that PP specimens modified with unmodified pigment reduce slightly the growing rate of the bacteria with respect to the results obtained for the control. However, a significant difference is found for the system prepared with the modified pigment.

Concerning the capability of IR shield of the painted plaques, it has been evaluated by total %R in the range VIS-NIR (300-2500 nm) by using an integrating sphere. The capability to reflect the wavelengths in NIR region confirm the capability to reflect the heat from the environment. An enhancement of 6.6% of reflectance within all the NIR range (750-2300 nm) was observed (see Figure 31).
LCA analysis for the automotive industry

LCA study has been conducted in conformity with the ISO 14.040 Series. Moreover, for each demonstrator, the LCA has been carried out through a comparison with a so-called “Base Case scenario” or “reference solution”, which can also be identified as the “Normal Production” material and component nowadays generally used in the automotive sector.

The Functional Units of the LCA analysis are the selected components, namely:

1. Fender of a Fiat Ducato 2014 for the application in vehicle exteriors, whose weight is about 2.5 kg. In the LCA of the Ducato fenders, the reference component (Base Case) is the one with the un-modified pigment, whereas the innovative “NANOPIGMY” solution is the fender with the new paint with the multi-functional Pigment 2.

2. External cover component of Fiat 500USA for the application in vehicle interiors, weighing about 320 g. In the LCA of the external cover component of 500USA the Base Case is the “Normal Production” one, with un-modified pigment in the mass-coloured polymer matrix, whereas the innovative “NANOPIGMY” solution is the component with the multi-functional modified pigment.

In the NANOPIGMY automotive applications, only the production phases of the fenders and external covers have been evaluated. The results obtained have been used for a final comparison of the different Base Case with their respective innovative solutions. The following graphs and the relative comments provide interpretation of such comparisons.

For the **fender painting**, a 14% decrease for Global Warming Potential (GWP) and 9% decrease for Primary Energy Demand (PED) are observed. This fact is due to the painting process optimisation, obtainable thanks to the introduction of the functionalised Pigment 2, which allows the elimination of some phases in the painting process.

For the **cover production**, a slight increase for GWP and PED has been obtained for production of a Fiat 500USA cover component with modified pigments into the PP. The slight increase of both impacts (3% increase for GWP and 2% increase for PED) in the cover with the innovative Pigment n. 4 is due to both, a mass increase in the component itself (associated to a higher amount of substances in the modified pigment) and, most of all, in an energy increase of about 10% in the injection moulding process. However, this slight increase
in the environmental impacts in the production phase might be sustainable in a life cycle perspective (the functionalised pigment 4 allows a higher and better product lifetime).

For the production of 1 kg of pigment 2 used in the application for painting automotive exteriors, a 53% increase for GWP and 56% increase for PED were observed. The considerable increase of both impacts in the Pigment 2 production is mainly due to two main reasons:

1. an extra electricity amount needed for the production of Pigment 2, estimated to about an extra 10% over the unmodified pigment, as also stated by Nubiola,
2. a higher environmental burden associated to the substances involved in the Pigment 2 production

However, looking at a life cycle perspective or, at least, at the application to the painting process in the automotive sector, taking also into account the productive volumes of commercial vehicles like Fiat Ducato, the introduction of this functionalized pigment might allow a considerable reduction of the environmental impacts in the “Normal Production” painting plants.

For the production of 1 kg of pigment 4 used for interiors application, a remarkable decrease of both impacts (12% decrease for GWP and 13% decrease for PED) is observed, mainly due to the lower environmental burden associated to the substances involved in the Pigment 4 production compared to the non-modified pigment, which also overcome the negative effect of the extra electricity amount needed for the production of Pigment 4, estimated to about an extra 10% over the unmodified pigment, as also stated by Nubiola, thus giving a positive overall balance for Pigment 4.

LCC analysis for the automotive industry

In the automotive industry, these pigments are to be incorporated into external paint and polymer components for the car interior. However, the scale of the polymer components being tested is too small to give life cycle cost improvements related to temperature reduction inside the car, so life-cycle costing is only being considered for the external paint application. The basis of the study is: “External painting of a Group A car (e.g. Fiat Panda) and the running costs of the air-conditioning unit over 8 year period”.

The benefit of using the NANOPIGMY paint is a reduction in the amount of energy used to run the air conditioning in the car. It can be greater than the engine power required to move a mid-sized vehicle at a constant speed of 56 km/h. According to a CRF test, the increase in fuel consumption is in between 17% and 30% depending on different vehicles. CRF assumes that an average of 24% is the increase of fuel consumption due to the use of conditioner (low regimes) in order to make the ambient temperature interior living conditions.

Unfortunately no detailed thermal modelling could be done to quantify the temperature reduction inside the car, so the life cycle cost calculations for the Alternative scenario have been carried out using a range of figures. The results of the life cycle costing analysis are shown in the chart in the following figure.

The Figure shows that the Alternative Case, with the NANOPIGMY paint is better solution, with a lower life cycle cost, in practically all the cases. Only a very slight reduction in air-conditioning use (much less than 1%) is required to offset the additional cost of the innovative pigment. To a first approximation, this break-even position can be estimated from the straight-line relationship between life cycle cost and reduction in air-conditioning use. Using the costs given above, the breakeven point is a 0.1% reduction in air-conditioning use.
Concerning the **REACH analysis** carried out into the project for the new developed pigments, it can be concluded that no significant differences are expected from the commercialization of modified pigments in comparison with the currently distributed pigments.
4.1.4. Potential impact (including the socio-economic impact and the wider societal implications of the project so far), dissemination activities and exploitation of results

The main results obtained in NANOPIGMY project have been grouped in four groups of results:

<table>
<thead>
<tr>
<th>Exploitable Results</th>
<th>Lead Partner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NANOPIGMY Pigments</td>
<td>NUBIOLA, TEK</td>
</tr>
<tr>
<td>2. NANOPIGMY Materials (interior paint, concrete, epoxy resin and thermoplastic masterbatches with different functionalities)</td>
<td>NUBIOLA, TEK, PIN, CHROMAFLO, PMB, ACCIONA, CRF</td>
</tr>
<tr>
<td>3. New processes to modify the functionality of the Nubiola’s pigments (coatings, embedding molecules,....)</td>
<td>TEK, NUBIOLA</td>
</tr>
<tr>
<td>4. Life Cycle Assessment</td>
<td>BSRIA</td>
</tr>
</tbody>
</table>

More specifically, 15 results coming from the project which have commercial significance and can be exploited as a stand-alone product, process, service, etc have been identified:

- Pigment 1: antibacterial and thermal storage
- Pigment 2: anti-corrosive and low-emissivity
- Pigment 3: self-cleaning and thermal storage
- Pigment 4: antibacterial and low-emissivity
- Material 1: New interior paints or colorants for antibacterial and/or thermal comfort applications (Pigment 1 in Paint)
- Material 2: New polymeric panels with thermal storage and antibacterial properties (Pigment 1 in Polymers)
- Material 3: New exterior paint with anticorrosive & low emissivity capability for automotive applications (Pigment 2 in Paint)
- Material 4: New mortars with self-cleaning and IR-high reflective ability for the construction of concrete walls (Pigment 3 in Mortar)
- Material 5: New thermoplastic masterbatches of plastic/pigments with antibacterial and low-emissivity capabilities (Pigment 4 in Polymer)
- Material 6: New cover frames for the car ratio or the air-conditioning systems with antibacterial & low-emissivity capabilities (Pigment 4 in Polymer)
- Material 7: New materials for construction with antibacterial & low-emissivity capabilities (Pigment 4 in Polymer)
- Process 1: New process to embed phase change materials in porous aluminium-silicate-based Nubiola’s pigments
- Process 2: New process to decorate aluminium-silicate-based Nubiola’s pigments with nanoparticles
- Process 3: New process to coat porous aluminium-silicate-based Nubiola’s pigments by using sol-gel technology
- Life Cycle Cost and Life Cycle Assessment System, as part of Pigment and Material development

More information about the innovativeness introduced compared to already existing Products/Services, the competitors of each result, the prospects and customers, the cost of the implementation and the estimated selling prices can be found in Table B2.
The initial exploitation plan of the industrial end-users has been established during the project and can be found in the section B (confidential). Some internal agreements have been signed between the partners of the project for the exploitation of the results. NANOPIGMY has 5 demonstrators as the main mechanism for demonstration of the materials prepared in the project: two different demonstrators have been defined for the automotive sector and three for the construction sector.

The socio economic analysis shows that adoption of NANOPIGMY pigments and materials across 10% of the total EU office and residential stock would deliver benefits in all areas:

- Increase in specialist jobs in pigment development and manufacture
- Decrease in incidences of ill health at work due to bacterial infection
- Decrease in the costs of building & maintaining, cooling, washing buildings of £4.64 billion over 100 years (equivalent to £280 million saved each year at 6% discount rate).

The savings calculated above already take account of the estimated increase in purchase price of the new products incorporating the NANOPIGMY pigments, so these are estimated net savings to the EU economy.

The table below summarises the socio-economic impacts described before and after the implementation of NANOPIGMY pigments and materials. All financial costs and benefits are given in terms of 100-year net present values in GBP using a 6% discount rate. Net present values are used to compare the economic impacts of alternative courses of action where these are based on activities occurring at different times in the future. To carry out a net present value comparison, a time period needs to be set during which any costs and benefits are to be compared, and also a figure is needed for the annual change in the value of money from one year to the next (this is called the discount rate and should not be confused with the inflation rate, which represents the change in prices from one year to year). The time period for the comparison between socio-economic impacts of using traditional materials and of using Nanopigmy materials has been defined as 100 years to be consistent with the time period used for the life cycle cost and the life cycle assessment calculations. There is no standard time period over which socio-economic impacts should be measured and this 100-year figure could be considered as arbitrary, so the net cost or benefit for each socio-economic impact has also been stated in annual terms. The actual figure for the discount rate can be thought of as the long-term difference between the cost of capital (interest rates on borrowings) and the rate of inflation. Clearly these figures are different for different organisations, companies and individuals. But a single rate has to be used, so the discount rate for the comparison has been defined as 6% as this is a middle-range figure between public and private sectors, between individuals and organisations and across the European economy. All costs and benefits have been quoted in GBP as UK sources have been used to estimate all the socio-economic costs and benefits in the analysis.

<table>
<thead>
<tr>
<th>Item</th>
<th>Current impacts</th>
<th>Anticipated impacts</th>
<th>Variance (+ve is beneficial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Employment in manufacture of raw materials, pigments, paint and polymer board</td>
<td>3,900 employed</td>
<td>3,920 employed</td>
<td>20 employees</td>
</tr>
<tr>
<td>Skill level of manufacturing employees</td>
<td>Mainly production</td>
<td>Cannot be quantified</td>
<td>Small increase in research, production</td>
</tr>
<tr>
<td>Extent of knowledge of use of nanotechnology</td>
<td>Operatives, some supervisory, research, production engineering, quality/safety</td>
<td>Cannot be quantified</td>
<td>Increase in knowledge for product manufacture and materials science</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>---------------------</td>
<td>------------------------------------------------------------------</td>
</tr>
<tr>
<td>Incidents of ill-health or sickness amongst building users caused by bacteria on internal walls</td>
<td>4,000 incidents per year</td>
<td>3,680 incidents per year</td>
<td>320 fewer incidents per year</td>
</tr>
<tr>
<td>Fossil fuel imported for cooling buildings</td>
<td>0.23% of EU consumption</td>
<td>0.2% of EU consumption</td>
<td>0.003% reduction in imported energy</td>
</tr>
<tr>
<td>Reduced cost of cooling buildings</td>
<td>£126 billion (100-year NPV)</td>
<td>£123 billion (100-year NPV)</td>
<td>£3 billion (100-year NPV), or £184 million per year (6% discount)</td>
</tr>
<tr>
<td>Cost of heating buildings</td>
<td>£147 billion (100-year NPV)</td>
<td>£147 billion (100-year NPV)</td>
<td>Nil</td>
</tr>
<tr>
<td>Cost of washing toilet and kitchen walls in office and domestic buildings</td>
<td>£14.2 billion (100-year NPV)</td>
<td>£13.1 billion (100-year NPV)</td>
<td>£1.1 billion (100-year NPV), or £66 million per year (6% discount)</td>
</tr>
<tr>
<td>Capital and maintenance costs for internal paint/polymer boards and external render</td>
<td>£126.1 billion (100-year NPV)</td>
<td>125.65 billion (100-year NPV)</td>
<td>£450 million (100-year NPV), or £27 million per year (6% discount)</td>
</tr>
<tr>
<td>Cost of washing external walls of rendered buildings (100 year NPV @ 6% discount rate)</td>
<td>£1.3 billion (100-year NPV)</td>
<td>£1.21 billion (100-year NPV)</td>
<td>£90 million (100-year NPV), or £5.4 million per year (6% discount)</td>
</tr>
</tbody>
</table>

On the other hand the project has used ‘standard’ dissemination mechanisms, as flyers, press releases, presence in media, congresses and scientific publications. A complete list of dissemination and exploitation actions is presented later in this document. The consortium has attended more than 14 exhibitions, fairs and conference to disseminate the project and its results. In addition, some press release and dissemination papers have been published.
This is an ongoing process beyond the end of the project. In fact, the validation of results has been achieved very late in the project, so the preparation of papers and publications based on these results will take some time.

4.1.5. Project contact
More information is available in www.nanopigmy.eu, or can be requested by writing to nanopigmy@tekniker.es or to the coordinator Pedro Villasante (p.villasante@nubiola.com). The list of participants and their web pages links are available through the project website.