PROJECT FINAL REPORT

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Project acronym: CuVito

Project title: Nano-structured copper coatings, based on Vitolane technology, for antimicrobial applications

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Name of the scientific representative of the project's co-ordinator[1], Title and Organisation:

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[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

4.1 Final publishable summary report

This section must be of suitable quality to enable direct publication by the Commission and should preferably not exceed 40 pages. This report should address a wide audience, including the general public.

Executive Summary (not exceeding 1 page).

The CuVito™ project was a collaboration between EU and Mexican partners under the Nanomaterials and processes call of the European Seventh Framework Programme (FP7). The over-arching project objective was to bring together Mexican mining products and European product development to produce a state-of-the-art copper nano-structured coating. The intended application of the coating was for use in anti-microbial activities within hospitals and other relevant applications. Anti-bacterial silver coatings are available; however they are not used in hospitals due to cost, effectiveness and durability. Copper offers a low cost, effective and environmentally friendly solution that could be readily adopted. The challenge that was identified was to retain copper nano-particles in a structure that provides antibacterial functionality, but prevents leaching.

The specific aims and objectives of the project were to:

- Develop a copper nano-particle production process capable of producing functionalised nano-particles cost effectively
- Functionalise silsesquioxanes with copper using Vitolane technology, targeting 90% functionalisation
- Produce a commercially acceptable coating
- Validate coating in a hospital environment with a target to reduce hospital acquired infections by10%.

Through close collaboration between the consortium partners, a cost-effective method for manufacturing copper nano-particles on a commercially viable scale has been developed that is currently being scaled-up from a laboratory environment to a batch production level. The CuVito™ consortium has developed a silsesquioxane structure, formed using Vitolane technology, in combination with various different approaches to functionalisation to develop copper nano-particle based products.

Protection of the results of the project is being conducted through six patent applications (3 in Europe and 3 in Mexico) whilst the following products have been identified for commercial exploitation:

1. Copper nanoparticle production.
2. Functionalised Stöber sphere (nanoparticle) production.
3. Additive system/coating solution.
4. Anti-microbial coating:
   a) Polyurethane based.
   b) Epoxy based.
   c) Acrylic based.
   d) Polyester based.
5. Copper nanoparticles integrated into polymer fibres.
6. Biosensors.

Summary description of project context and objectives (not exceeding 4 pages).

The European Centre for Disease Prevention and Control (ECDC) has calculated that the annual number of patients in the EU with at least one hospital acquired infection can be estimated at 4.1 million patients, equivalent to one in twenty hospitalised patients. Since patients sometimes acquire more than one infection during the same hospitalisation, the yearly number of acquired infections is estimated at 4.5 million. Every year, approximately 37,000 deaths are thought to be caused directly by hospital acquired infections; an additional 110,000 deaths occur annually in which such infections are a contributory factor (1).

Copper and silver nanoparticles exhibit antimicrobial behaviour which may allow materials to be developed that prevent the spread of these infectious agents. Whilst silver based coatings are available they are considered to be expensive, and only work under a narrow range of conditions.

The challenge for copper coatings is to restrain the copper nanoparticles (CuNps) in a structure that provides antibacterial functionality, but prevents leaching of copper into the environment. The CuVito consortium believes that the silsesquioxane structure, formed using Vitolane technology, can provide the answer. The silsesquioxanes will effectively bind the CuNp to the substrate of interest and prevent it from accidental release into the environment, whilst ensuring it is available to release ions which will provide the antimicrobial characteristic.

Silsesquioxanes have been available for some years but at a prohibitively high cost, due to the complexity of manufacture. Vitolane technology represents an alternative, cost effective patented production route which can be readily tailored to incorporate the most appropriate functional groups to bind to the copper to textiles which have been selected as target substrate within the CuVito project. This project is a joint European-Mexican project aimed at developing new products for the Mexican mining industry. The project partners are:

Mexican Partners:
Centro de Investigacion en Quimica Aplicada – CIQA
University of Guanajuato
Metal Técnica S.A. de C.V.

European Partners:
TWI Ltd (UK)
Institut Fuer Neue Materialien (Germany)
Cyanine Technologies (Italy)
Thomas Swan (UK)

The specific aims and objectives of the project were to:

- Develop a CuNp production process capable of producing functionalised nanoparticles cost effectively.
- Functionalise silsesquioxanes with copper using Vitolane technology, targeting 90% functionalisation.
- Produce a commercially acceptable coating.

- Validate coating in a hospital environment to reduce hospital acquired infections by10%.

The properties required for the antimicrobial coating were considered based on criteria falling into the following categories:
- Scientific.
- Technological.
- Environmental.
- Industrial.

The initial focus of the project was the identification of the most promising technical routes to the fabrication of CuNps, including cost analysis. A comprehensive review of CuNp synthesis methods has been carried out. The aim was to identify a low cost production route for CuNps which are suitable for a further functionalisation.

Ranking of the nanoparticle synthesis routes was then undertaken according to parameters such as:

- Scalability.
- Risk/hazard.
- Reaction time.
- Cost/availability of the precursors.

Laboratory scale fabrication was undertaken and the CuNps fully characterised using a range of analytical methods including transmission electron microscopy, X-ray diffraction and Fourier Transform Infra-red spectroscopy. Transfer of the synthesis methodology to the industrial partners has occurred and been verified using the same analytical techniques. Scaled-up fabrication has also occurred and the analysis of the resultant nanoparticles is underway.

The fabrication of the CuNps was complemented by the determination of the feasibility of functionalising CuNps using silsesquioxanes and alternative materials such as silane coupling agents. With the target application of textiles as the focus of the project a number of silsesquioxanes have been designed and then fabricated at the laboratory scale for examination and use in functionalisation trials.

The achieved progress was in line with expectations and can be summarised as:

- CuNps have been manufactured – multiple synthesis routes have been explored.
- Scale-up trials progressing to develop a process suitable for large scale manufacturing (100 litres).
- Functionalisation methods have been identified and trialled.
- Scale-up of functionalisation methods has been studied.
- Samples of coated textiles have been produced.
- CuNp impregnated fibres have been produced.
- CuNp coatings onto aluminium have been produced.
- CuNp coatings onto stainless steel have been produced.
- Target market of medical textiles has been identified.
- Commercialisation opportunities with large Mexican materials fabricator are being explored.

- Commercialisation opportunities for specific CuVito products are being explored.

The following potential impacts were achieved from the CuVito project:

1. The creation of a novel copper-silsesquioxane structure using Vitolane technology to give greatly enhanced properties allowing the economic use of copper in biocidal coatings.

2. The CuVito project has created new knowledge in several areas:
    - Functional silsesquioxanes produced using the Vitolane process.
    - Stable CuNps with functionality to bond to the silsesquioxanes.
    - A production process capable of producing the CuNps.
    - An integrated nanocomposite coating ready for commercialisation (polymer/glass matrix).
    - Validation data from hospital field trials.

3. The rapid, effective and permanent biocidal treatment of surfaces across a number of markets, including healthcare and food manufacture and processing.

4. The CuVito product holds enormous potential as a safe, non-toxic alternative to silver based coatings and traditional biocides in the healthcare arena, for work surfaces, medical devices and potentially even flooring and seating in operating theatres, etc.

5. The CuVito project aims to ultimately reduce hospital acquired infections by 10%.

A description of the main S&T results/foregrounds (not exceeding 25 pages)

The main scientific and technological (S&T) results and corresponding foreground intellectual property was developed within specific work packages by the consortium partners. The S&T work packages:
WP 1: Technology Design
WP 2: Synthesis of Nanoparticles
WP 3: Functionalisation
WP 4: Coating Formulation
WP 5: Coating Deposition
WP 6: Coated Sample Evaluation

At the start of the CuVito™ project a technology review was undertaken in order to identify and design suitable process routes for the manufacture of copper nanoparticles and systematic experiments. This activity was undertaken as part of work package 1 'Technology Design'. This involved the design and development of a process route identifying the key process steps from ore extraction to final coating production. These steps were then translated into a systematic experimental approach with tasks being allocated to the relevant project partners.

The approach taken was to design the coating considering the properties the coating must exhibit, then considering in order curing, coating deposition, formulation, functionalization, and nanoparticle synthesis. Each of the processing steps were further sub-divided as required. The properties required for the antimicrobial coating were considered based on criteria falling into the following categories:

- Scientific
- Technological
- Environmental
- Industrial

The properties of the coating that were considered included:

- Anti-microbial performance
- Morphology
- Chemical characteristics
- Mechanical/physical characteristics
- Copper ion release rate
- Handling issues
- Cleaning
- Appearance
- Cost

A general process route was designed and included:

- Nanoparticle fabrication route definition
- Functionalisation method selection
- Commercial formulation identification
- Coating method determination

During the design of the process route it was necessary to select a generic substrate for experimental characterisation. As a result of market data and discussion within the project consortium it was agreed that the Mexican partners would focus on the functionalisation of synthetic fibers and the European partners would focus on cotton. In addition, coating development was pursued using both aluminium and stainless steel substrates. Once the substrates had been identified, it allowed the project consortium to establish a functionalisation route design and selection of potential candidate model systems. In turn, it was then possible to determine likely deposition methods, formulation boundaries, the framework for likely characterisation and evaluation tests of the final product.

As part of the activities of work package 1 a life cycle analysis was undertaken using GaBi software to try and benchmark the project technology. Four routes were considered for the application of copper nanoparticles (CuNP); aluminium, steel and cotton substrates with a coating containing CuNp applied to the top surface, and Cu/polypropylene textiles produced by melt blending the copper into the polypropylene at the fibre formation stage.

Detailed consideration was given to the manufacture of the copper nanoparticles, to the additive manufacture and copper functionalization and to the integration of the copper into thermoplastics such as polypropylene. For the LCA, no transportation data was included in the modelling. Data for the LCA was generated via literature surveys.

It was found that a significant amount of the environmental impact for different product cases were attributable to the nanoparticle synthesis stage. The nanoparticle synthesis was examined only at the laboratory scale, and it is anticipated that scaling up the process is likely to improve this result as would the use of recycled feedstock. The conclusions of this study were that:

- The Global Warming Potential (GWP) of the cotton textile has been calculated to be 23.4kgCO_2e/kg, and 8.4kgCO_2e /m^2 assuming a 200g/m^2 weight of cotton fabric.
- The GWP of the polypropylene textile has been calculated to be 133.5kgCO_2e/kg and 5.3kgCO_2e/m^2 assuming a 40g/m^2 weight of polypropylene fabric.

As part of the activities of work package 1 a health, safety and environmental assessment was undertaken by the project consortium. A review of the regulatory and legislative framework for nanomaterials and nanotechnology was completed. This identified that there are a number of public bodies involved in the development of new practices, procedures, standards, regulations and legislation for new materials and new working practices. These bodies exist at the national level, at the EC level and also globally. The jurisdiction of these bodies is, unfortunately, not clear. There is also the added complexity between those bodies whose remit is to provide information and guidance and those whose role is to police the regulations.

A full health, safety and environmental assessment for the use of nanomaterials must therefore show that due diligence has been undertaken and the most relevant guidance has been identified and included. This activity had three primary elements:

- Health, safety and the environment regulation
- Standards
- Operational procedures

The conclusion of this investigation was that the standard approaches for risk assessment and material disposal can be used for nanomaterials and, in line with normal practice, need to be specific to the materials and the operational environment. A number of guidance documents and draft standards to allow this specificity to be achieved have been highlighted. It was concluded that specific products being produced under the CuVito™ project can therefore be provided into the market place with the requisite MSDS and risk assessment information that could be produced by the supply side project partners based on compliance with existing legislation.

Synthesis of Nanoparticles

The synthesis of copper nanoparticles was undertaken within work package 2. This activity identified potentially suitable precursors, chemical processing and synthesis methods with the aim of selecting the most appropriate method for low cost, medium volume production of copper nanoparticles. To select the most suitable precursor for fabrication of copper nanoparticles, parameters such as cost and amount used, availability and handling cost were studied to select the appropriate precursor. $CuSO_4$ and $CuCl_2$ were down selected as the most appropriate precursors.

To find a nanoparticle synthesis route that would allow a cost effective mid-scale production, Metal Técnica and INM first set up an overview of various syntheses that could be used to produce copper nanoparticles in general. Using various evaluation criteria like yield, precursor costs, equipment costs etc. this enabled the number of possible methods to be narrowed down to those that would fit the demands. Synthesis routes that were considered included laser ablation, ball milling, photo-reduction, thermal reduction and chemical reduction. From the preliminary investigations, thermal reduction and chemical reduction were selected for the investigation of the thermal decomposition of an organic copper precursor. Transmission electron microscope (TEM) images of copper nanoparticles can be seen in Figure 2.

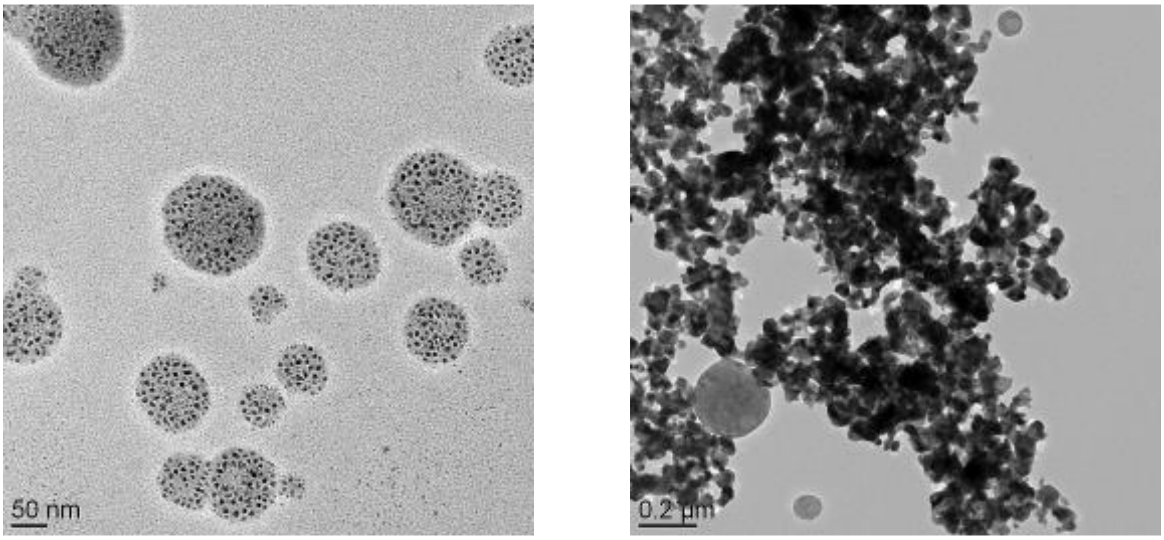

Figure 1 TEM images of stabilised Cu nanoparticles manufactured using thermal decomposition. Left: use of higher concentrated precursor; right: lower concentrated precursor.

Investigation of the CuNps after manufacture found that it would be necessary to develop a separation and purification process for the purification of the CuNps. Several methods for the purification of the copper nanoparticles were explored by Metal Técnica and INM to allow the large scale purification and the removal of the most of the chemical reducing agent. It could be shown that the addition of sodium carbonate during the washing steps in the usually used centrifugation/redispersion washing procedure used at lab scale drastically reduces the amount of organic carbon from values above 20% by weight to values below 0.2% by weight. Another method of purification that was investigated was a tangential cross-flow system, which allows a simple and easily scalable setup. Tests at INM were found to show promising results: The carbon content could be reduced to a sixth compared to a regular dialysis.

In order to scale up the CuNp manufacturing process, INM and Metal Tecnica agreed a fabrication protocol which was replicated in the prototype scale up rig in Metal Tecnica´s facilities. Initially fabrication was undertaken at the small scale (500ml) to confirm reproducibility and establishment of full transfer of the technology followed by fabrication of a 20 litre batch. Characterization of the small scale batch confirmed that the obtained particles were of 15 nm with spherical morphology and a homogeneous distribution. An illustration of the scale-up reactor can be seen in Figure 3.

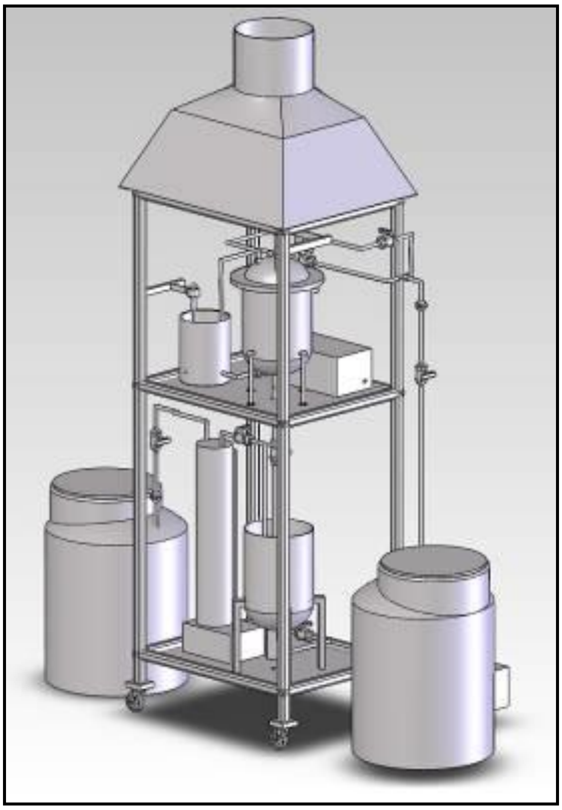

Figure 3 Illustration of the scale-up reactor being built by Metal Tecnica.

Initial evaluation of the particles made by thermal reduction and chemical reduction was undertaken by the University of Guanajuato. The antibacterial properties of the particles were compared with commercial copper and silver nanoparticles. Analysis of CuNPs was primarily performed by TEM and x-ray diffraction (XRD) studies. Repetition of testing found that $CuSO_4$•$5H_2O$ was a suitable precursor to produce spherical copper nanoparticles at larger scale with a narrow size distribution between 5 and 20 nm, depending on synthesis conditions. INM conducted several tests on the chemical reduction routine to see the effect of various synthesis conditions on the nanoparticles. Precursor concentrations were varied as well as ascorbic acid concentrations, synthesis temperature, stirring speed etc. The optimization results were given to Metal Técnica for the setup of a large-scale prototype for this synthesis. In all syntheses done during the optimisation, Cu was obtained, as XRD measurements corroborate. TEM analyses showed that the syntheses yielded spherical nanoparticles in the range of 5 to 20 nm, depending on the conditions. The yields varied, depending on various parameters, like the amount of precursors used or the reaction temperature.

The results obtained by INM allowed Metal Técnica to set up the prototype with the most promising conditions for a large scale production. The particles produced in the optimization process performed by INM were tested at UOG for their antibacterial properties and it was found that their anti-bacterial properties correlated with the carbon content of the nanoparticles.

Thomas Swan Ltd has carried out provisional commercial assessments of the copper nanoparticle production route. INM have supplied Thomas Swan with several potential outline laboratory synthetic pathways to produce CuNps. The cost analysis determined that the chemical reduction route for the manufacture of copper nanoparticles is competitive with commercially available products.

Functionalisation

At the outset of the project it was recognised that one of the primary S&T challenges would be to functionalise the CuNps such that they would be compatible with the carrier system in which they would be used e.g. polymer resins. The work that was performed needed to take account of the different substrates e.g. textiles and metal surfaces as the requirement for treatments on textiles is profoundly different to those of hard surfaces. The project partners agreed that the two generic activities focussing on functionalisation would address different aspects of textile treatments. Specifically, the European partners would develop functionalisation methods aimed at the treatment of natural (cotton) textiles, whilst the Mexican partners would develop treatments for the incorporation of nano-copper into synthetic textiles.

It had been established that treatments for natural textiles need to be water based to be compatible with conventional processing methods. They also need to ensure that the treatment does not affect the feel or flexibility of the textile whilst imparting the additional attribute required. Coatings and textile treatments can generate either very dilute film-forming compositions, which wet onto each filament, but are very deposition method sensitive, or allow the discrete deposition of active agents. To achieve these aims a design review for the silsesquioxane functionalisation molecule was undertaken. A number of silsesquioxanes were designed and then fabricated at the laboratory scale for examination and use in functionalization trials. The specific requirements of the silsesquioxanes were to: a) bond to the copper nanoparticles, b) bond to the surface of the cotton textile, c) have either a film forming capability or to have no film forming capability, d) be dispersible in the appropriate liquid vehicle.

The approach taken was to fabricate silsesquioxanes of increasing complexity once an understanding of the synthesis method of simpler functionalities had been established. In the first instance the key functional groups to impart the required attributes needed to be identified, and a number of candidate silane coupling agents were selected as candidates. On the basis of cost, handling hazard, commercial availability and compatibility with the Vitolane process (which demands low pH constituents) the (3-Mercaptopropyl)trimethoxysilane was selected as the most promising candidate.

Laboratory trials were then undertaken to establish a route to the manufacture of a silsesquioxane made solely from this silane, called the thiol-silsesquioxane. Once the route to this silsesquioxane was established, the method was provided to Thomas Swan for scale-up consideration. Laboratory scale synthesis of the silsesquioxane was undertaken and a range of analytical and characterisation methods were completed. Trials with the thiol-silsesquioxane showed successful functionalization and so this method was chosen as a possible candidate for the large-scale production.

The thiol silsequioxane was determined to have an average molecular weight of 1115g/mol. This was derived from its HPLC retention time, the retention signal is given below in Figure 4. This molecular weight indicates that the silsesquioxane is likely to have an average structure containing seven silicon atoms, based on the average molecular weight of the T(2) species of 161. This is broadly consistent with a trisilanol cubic septomer type silsesquioxane.

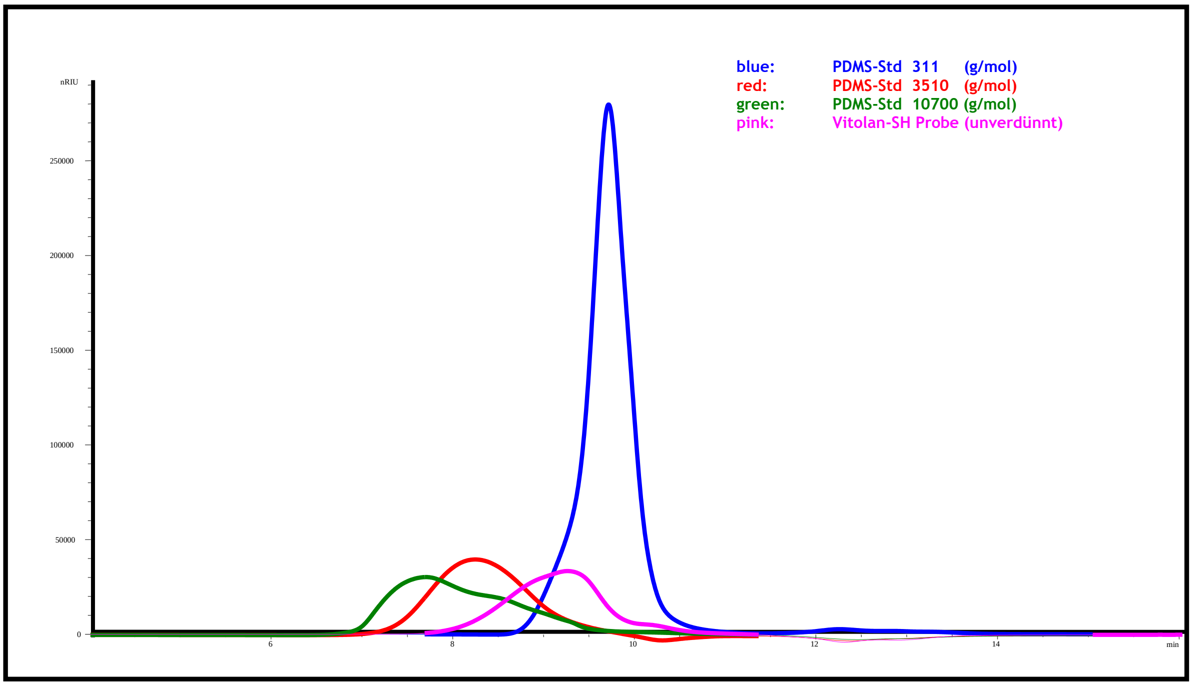

Figure 5 HPLC retention signal of the mercapto functional silsesquioxane, the silsesquioxane signal is pink, the other signals are various polystyrene standards

In addition, two further silsesquioxane fabrication procedures were developed, one of these generated a dual functional silsesquioxane, with the capability of bonding to both copper and cotton textiles, the third silsesquioxane had both these attributes in addition to an additional functional group that would reduce excessive bonding to either of these materials and would allow controllable quantities of the silsesquioxane to be deposited onto the copper nanoparticles.

The multiple functional group silsesquioxanes were then exposed to copper nanoparticles and it was demonstrated that thiol containing silsesquioxane yielded copper colloids in organic solvent, whereas non-thiol based silsesquioxanes gave copper ions via a dissolution mechanism. The TEM of the resultant nanoparticles is shown in Figure 6. This shows that the particles are incorporated in an amorphous matrix and are agglomerated, but were capable of being dispersed in ethanol, figure 7.

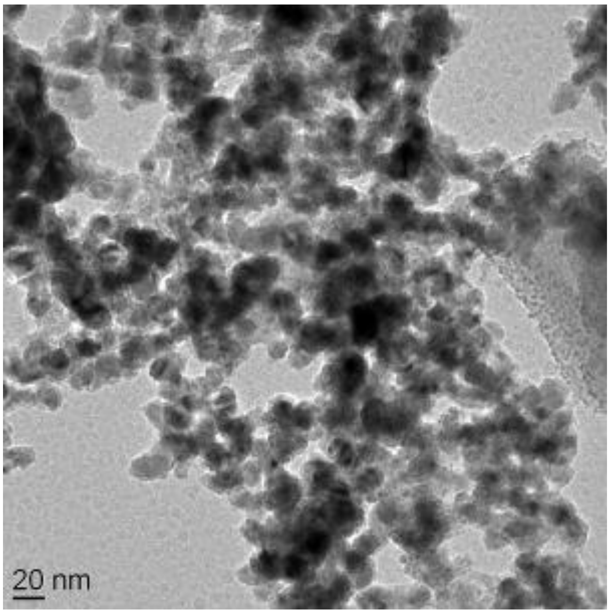

Figure 6 TEM images of thiol-silsesquioxane covered Cu nanoparticles

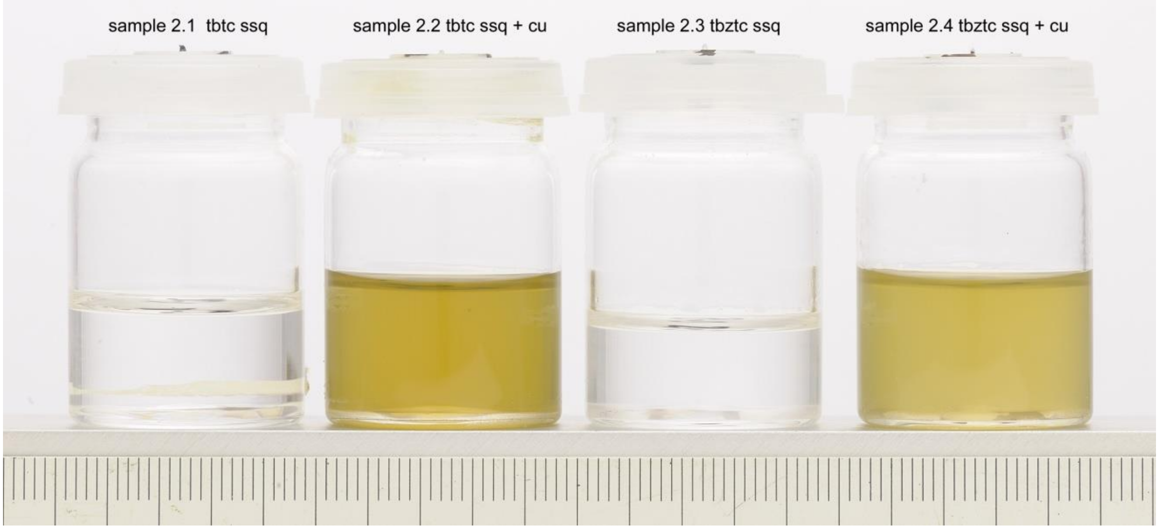

Figure 7 Photograph of dual and triple function silsesquioxane without and with exposure to copper nanoparticles. The coloured liquids have both been exposed to copper. The two dual functional silsesquioxane samples are on the left of the image, the two triple functional silsesquioxane samples are on the right of the image.

The thiol based silsesquioxane/copper colloidal suspensions were successfully deposited onto cotton textiles, figure 8.

Figure 8 Photograph of cotton textile impregnated with a triple functional silsesquioxane/copper nanoparticle and cured at 120°C for 5 minutes.

Process parameters for the scale up of these silsesquioxanes were provided to Thomas Swan and preliminary costs for larger quantity manufacture were generated. As part of this cost analysis, raw material assessments have made on the basis of Far East vs. Western supply base and also purchase quantity. Brief assessments of supplier company size and security of supply have also been carried out. This data was then fed into cost models for raw material cost comparisons.

In addition to the functionalisation of CuNps undertaken using silsesquioxanes, alternative routes to functionalization of copper nanoparticles and copper oxide nanoparticles (nCuO) by different methods was successfully completed. Modification and functionalization by silanes, oxidative hydrolysis and nitrogen ligands were carried out simultaneously aiming to obtain a perfect control of size and morphology of the nanoparticles and formation of coating on particle surface. In addition, the inclusion of CuNps in acrylic coatings by surface modification using a plasma treatment was successfully completed. Successful demonstration of functionalisation was achieved by the production of synthetic textile fibres containing different loading levels of copper, see Figure 9.

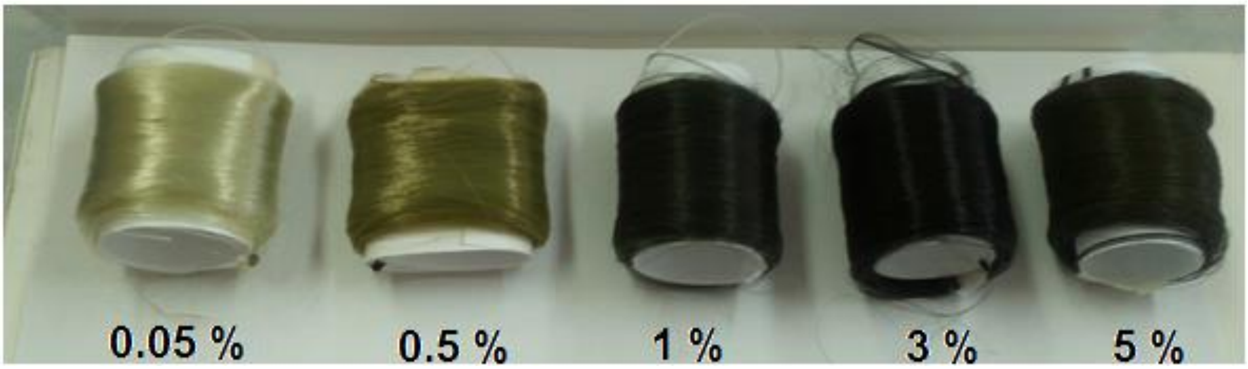

Figure 9 Polypropylene/copper nanoparticles threads with different amounts of nanoparticles

Coating Formulation

Following the manufacture and functionalisation of the CuNps it was necessary to consider the development of suitable formulation protocols such that the CuNps could be applied into their intended applications. Several application methods for the textile functionalisation exist, such as roll-to-roll, immersion or ink-jet processing, as used for the dyeing procedures. Also, a plasma treatment is possible. The identification of the best way for implementation into currently used manufacturing processes was completed by Pianeta. A water-borne coating formulation was specified as a treatment for textiles, this was to allow industrial adoption based on the common practice of water based inks with a solid content of 2-10% with curing being thermal, typically 150°C for 5 minutes. For the polypropylene textiles, the approach adopted was to incorporate the copper nanoparticles into the polypropylene melt blend prior to fibre spinning, hence no coating model system was identified.

An epoxy resin system as a model coating for steel substrates was selected. Araldite CY 179 is an extremely low-viscosity, reactive diluent free matrix system with a long pot life. This resin displays very good post cure temperature resistance and exhibits good adhesion to steel substrates. A generic model system for an abrasion resistant coating on aluminium was identified. This coating formulation had been developed by Sartomer and consisted of UV curable acrylate chemicals. The coating formulation was solvent-free and rapid curing under UV irradiation and so was selected on the basis that it belonged to the most environmentally responsible class of coating formulations. This formulation also did not require a primer treatment and produced an abrasion resistant surface film on aluminium.

Coatings for steel

Copper nanoparticles (CuNP) were added into Araldite CY 179, a diluent free matrix system in the range of 0.1 to 2% by weight. In some cases, surface modifiers were tested to potentially increase the redispersibility of the nanoparticles. The particles were stirred for several hours, then a UV initiator was added. Stainless steel substrates and glass were coated using spiral bar-coaters with 10-30µm or applicator frames with 0.1 to 0.5mm. In the case of coatings for aluminium, a number of different formulations were considered, fabricated and deposited on aluminium substrates.

Coatings for textiles

For the controlled application of CuNP onto textiles, Pianeta proposed ink jet technology as this would allow a controlled distribution on the cotton fabric. Therefore, it was necessary to develop an appropriate ink based on the thiol-silsesquioxane developed earlier in the project combined with either water or isopropyl alcohol. The visual appearance of the recovered supernatant liquids was an amber coloured liquid whose depth of colour increased as the amount of copper and thiol silsesquioxane in the parent mixture respectively increased and decreased.

Additional activity to functionalise the copper nanoparticles were undertaken. These were based on the need for a bidentate ligand, one that could couple to the copper but also to the substrate (cotton). An alternative approach was adopted were separate silica nanoparticles were manufactured, functionalised with a thiol silsesquioxane and then combined with the copper nanoparticle, shown schematically in Figure 10.

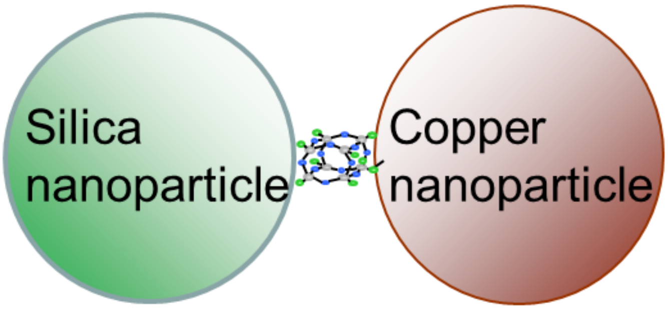

Figure 10 Schematic illustration of a functionalised copper and silica nanoparticle.

A number of ink formulations were prepared based on this approach, two were water based and two were solvent based and can be seen in Figure 6.

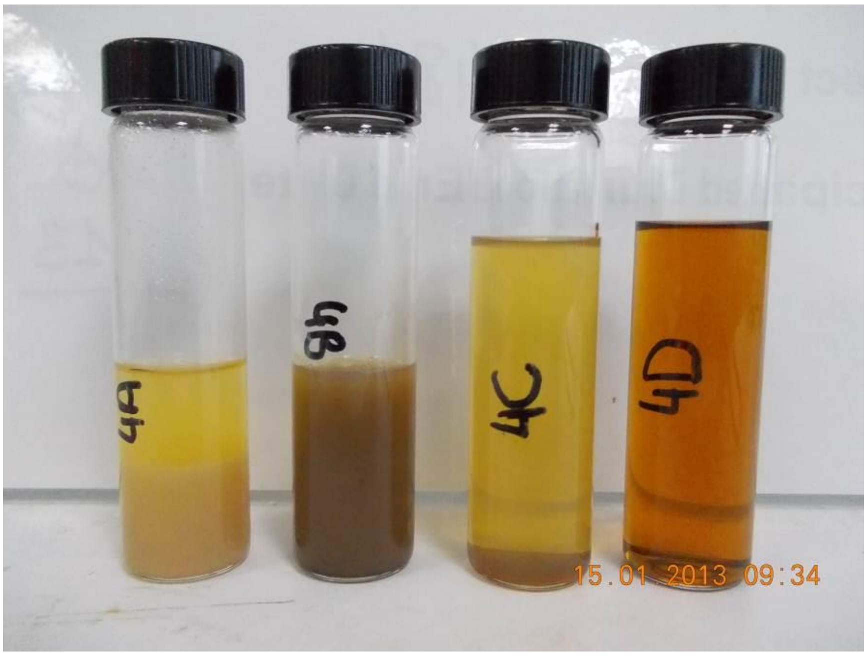

Figure 11 CuVito™ Ink for deposition trials.

A number of methods were used to incorporate copper nanoparticles into polypropylene, these included and included Surface plasma modification of copper nanoparticles with different acrylic monomers: acrylic acid (AA), methyl methacrylate (MMA) and acrylonitrile (AN). During plasma modification, copper nanoparticles were coated with a thin film (5nm) of polymer. Preparation of acrylic/copper and epoxy/copper nanocomposites by photo-polymerization was completed by mixing acrylic or epoxy monomers with a photoinitiator and copper nanoparticles. After ultrasonic agitation the mixtures were placed into Teflon moulds and exposed to UV light during 3 minutes.

Different amounts of commercial copper nanoparticles into polypropylene was carried out by melt extrusion assisted by ultrasound. The polypropylene threads obtained for different concentrations of copper nanoparticles can be seen in Figure 9. In this case, the presence of copper nanoparticles generated a green coloration, which increased in intensity with copper concentration.

Manufacturing considerations based on the latest understanding of the process flow for the production of copper nanoparticles, silsesquioxane coupling agent and a new silica nanoparticle support agent were evaluated. The materials cost base, process flow considerations and likely batch time reviews were considered. The additive design went through an iterative approach to produce a final refined methodology.

The manufacturing routines are considered as both feasible and suitable for adoption within the manufacturing capability of the CuVito project partners. Based on the assumption that the additive is supplied in aqueous suspension at approximately 1% loading, the costs would be allow for a final product price of €12-15/litre Discussions with those in the textile industry suggest that water borne treatments for dyeing and to provide hydrophobic characteristics are typically sold in this price range. On this basis, it is considered that a commercially viable product can be manufactured and priced at level that would be acceptable to the market place.

Coated Sample Evaluation

The University of Guanjuato completed anti-microbial testing of a range of different Cu and silver nanoparticle based materials. Silver nanoparticle material is being investigated in order to provide comparative data with existing products in the marketplace.

The antimicrobial activity of polypropylene/silver (PP/Ag) and polypropylene/copper (PP/Cu) nanocomposites has been investigated in order to evaluate the effect on this activity when the nanoparticles were exposed by argon plasma treatment. The antimicrobial properties were evaluated on pathogenic bacteria *S. aureus* and *P. aeruginosa*. Antibacterial activity against *S.aureus* after different time of interaction with untreated Cu nanocomposites and plasma treated (1, 3 and 6 hours) has been demonstrated. The antimicrobial activity was related directly to the amount of nanoparticles in the polymer. Plasma treated nanocomposites presented a significant increase of their antimicrobial activity, due to the fact that nanoparticles were directly exposed to the surface by the argon plasma treatment.

By comparison antimicrobial activity against the Gram (-) *P. aeruginosa* presenting a higher antibacterial effect than on *S. aureus*. The same effect is observed were the plasma treatment increases their antimicrobial activity. According to these results, the nanoparticles exposure at the surface of polymer nanocomposites by argon plasma treatment was decisive to obtain high antimicrobial properties at lower contact time, thus enhancing the surface properties and the functionality of polymer nanocomposites.

The antimicrobial activity of a number of additive samples containing Cu nanoparticles synthetized by INM and functionalized using mercapto silsesquioxane by TWI have been investigated. Commercial functionalized Cu nanoparticles were also evaluated. All the samples were prepared in water as well as in isopropyl alcohol (IPA). Antibacterial activity against *S. aureus* for the samples containing Cu nanoparticles without mercapto silsesquioxane prepared in water was evaluated. The commercial Cu nanoparticles had low antimicrobial activity even after 60 min of interaction reaching a maximum of 39 % of antimicrobial activity against *S. aureus*. The sample 44 corresponding to the nanoparticles synthetized by INM showed higher antimicrobial activity than the commercial ones, reaching 95%.

The antimicrobial activity against *S. aureus* was evaluated from a sample denominated TSS4b/S/INMCu (the water based Stöber sphere/thiol/INM Cu ink). This sample was used to soak small pieces of cotton cloth.. It seems the antimicrobial activity was time dependent. After 6 hours of interaction the antibacterial activity was 95%.

A comparison of the anti-microbial properties of silver or copper containing polypropylene fibres can be seen in Figure 12. It is evident that the copper containing fibres developed within the CuVito™ project show better or equivalent anti-microbial activity compared to silver containing fibres.

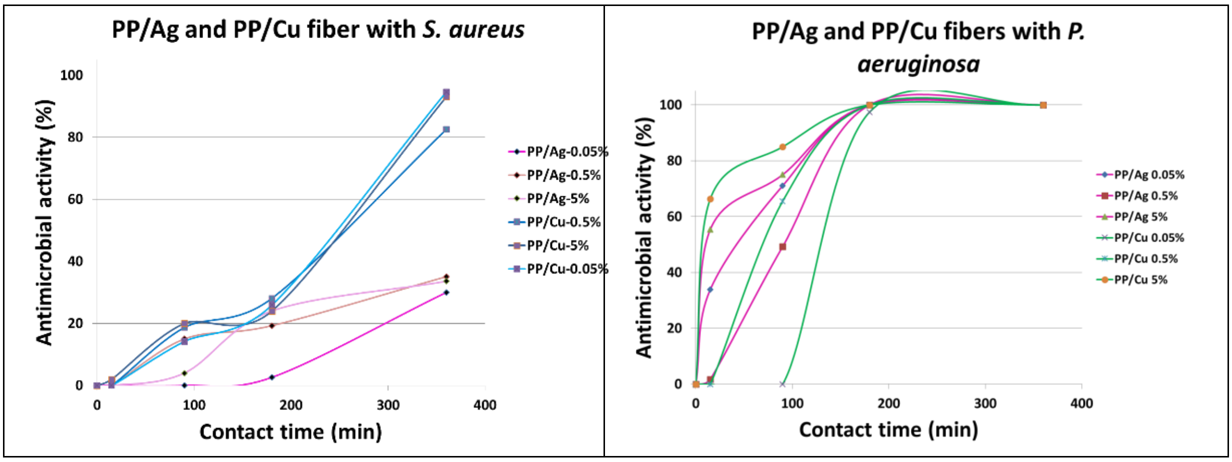

Figure 12 Antimicrobial activity of PP/Cu and PP/Ag fibres in contact with *S. aureus* and *P. aeruginosa*.

Work is on-going to validate the CuVito™ project results in a medical environment.

The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results (not exceeding 10 pages).

The intended impact of the CuVito™ project is to reduce hospital acquired infections and develop anti-microbial treatment for a wide range of different markets. Examples of these markets can be seen in Figure 13. Further economic impact is anticipated through the development of the foreground intellectual property developed within the project. Six patents are currently being applied for which will allow the project partners to protect the exploitable project results

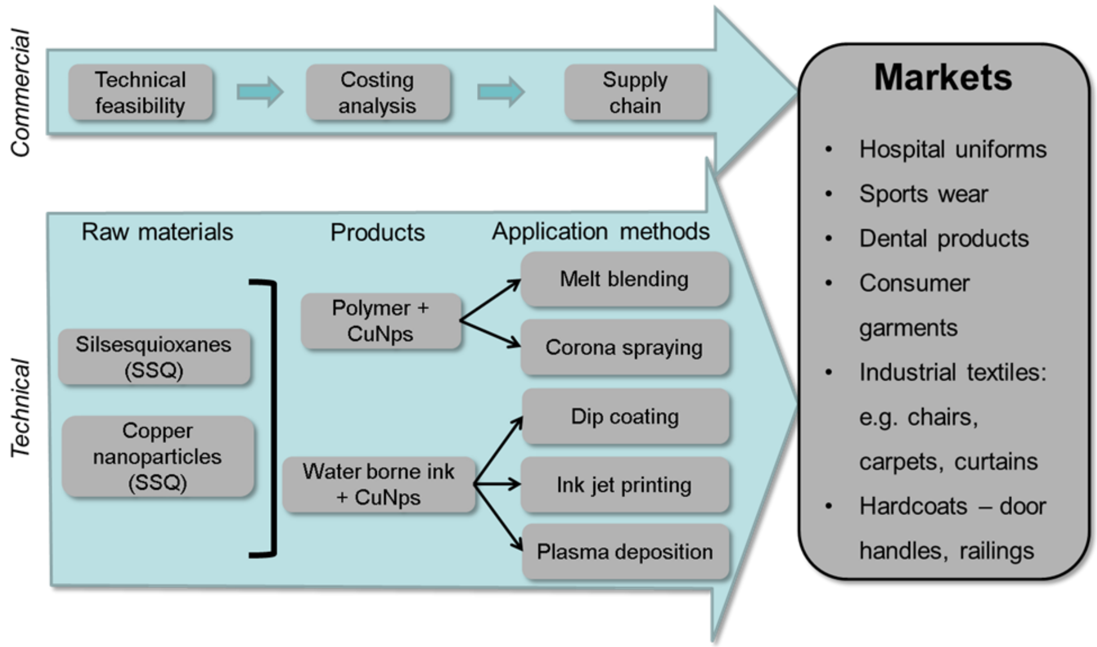

Figure 13 CuVito™ technology and exploitation markets.

The CuVito™ project has demonstrated that CuNPs can be incorporated into a number of different carrier systems and still impart anti-microbial activity. Currently exploitation of the CuVito™ technology is being explored through three specific routes. These are:

1. Copper nanoparticle production.
2. Anti-microbial coating:
   a) Polyurethane based.
   b) Epoxy based.
   c) Acrylic based.
   d) Polyester based.
3. Copper nanoparticles integrated into polymer fibres.

As the exploitation routes above are developed the following products have been identified for exploitation by the CuVito™ project consortium:

- Fibres for textile products
- Ink for textile products
- Nanoparticles
- Multi-functional additive system

- Coatings for surfaces e.g. finger panels, hand dryers

The exploitation of the production of copper nanoparticles is being led by Metal Tecnica through the development of the pilot-scale reactor plant for the low cost manufacture of CuNps. In order to exploit the project results, Metal Tecnica is considering the creation of a new company specifically to exploit nano-technology based products. An initial product currently under consideration is a paint additive. The exploitation of anti-microbial coatings based on polymeric carriers is being pursued by both the Mexican and European project partners. CIQA is currently in the process of exploitation of the polymer fibres containing copper nanoparticles and have developed preliminary datasheets to be distributed into potential markets.

In order to assist with both project exploitation and dissemination activities a project logo was developed to assist with brand development. This can be seen in Figure 14. The project consortium is also using trademark with the name ‘CuVito’.

Figure 14 The CuVito™ project logo.

Dissemination

Project dissemination activities have been on-going throughout the duration of the project. This has primarily been through the generation conference posters and presentations and attendance at such events.

As part of the final CuVito™ project meeting that was scheduled to be in Mexico, the project consortium agreed to co-ordinate the meeting timing and location with the XXII International Materials Research Congress (IMRC 2013), August 11-15 in Cancun, Mexico. As part of this activity the project consortium hosted a 1 day symposium with the title ‘Nanotechnology-Enhanced Coatings’. The description of the symposium reads as follows:

> ‘Advanced high-performance coatings have been the focus of considerable research activity due to their considerable promise for use in a range of industrial applications. The design and synthesis of chemically complex, hierarchical structural arrangements pose considerable challenges in terms of how these materials are described, characterized, fabricated, tested and developed into commercial products.
>
> This symposium will bring together physicists, chemists and materials scientists from academic, technology-providing and industrial organizations to accelerate progress in this field. The key aim of the symposium is to facilitate discussion and debate to identify the primary areas for focus to allow more rapid transition from the laboratory to industrial acceptance while also ensuring that the necessary

depth of understanding of the physics and chemistry of material development is achieved.

The key foci of the symposium will be provided by the invited speakers who will aim to provide a link between the academic and industrial spheres of new materials innovation. The mechanisms of materials synthesis, and the description of complex structures and how they relate to functional performance and manufacture at viable scales, will be the central themes for this symposium. Tutorials on materials synthesis and industrial adoption will ensure that these aspects are central to the event. Workshops will be held to facilitate dialogue between industrial and academic participants. Dissemination of the talks and outputs of the workshops will be undertaken to ensure that the widest possible audience receives great value from the symposium.

Symposium topics to be addressed include (but are not limited to):

Barrier and protective coatings
Biocompatible and bioactive coatings
Nanostructured coatings
Industrialization challenges for new materials and coatings'

A total of 19 oral presentations were made and 11 posters were submitted on the same topic to the evening poster session. Approximately 40 attendees were present for each of the symposium sessions. Two examples of posters from the project can be seen in Figures 15 and 16.

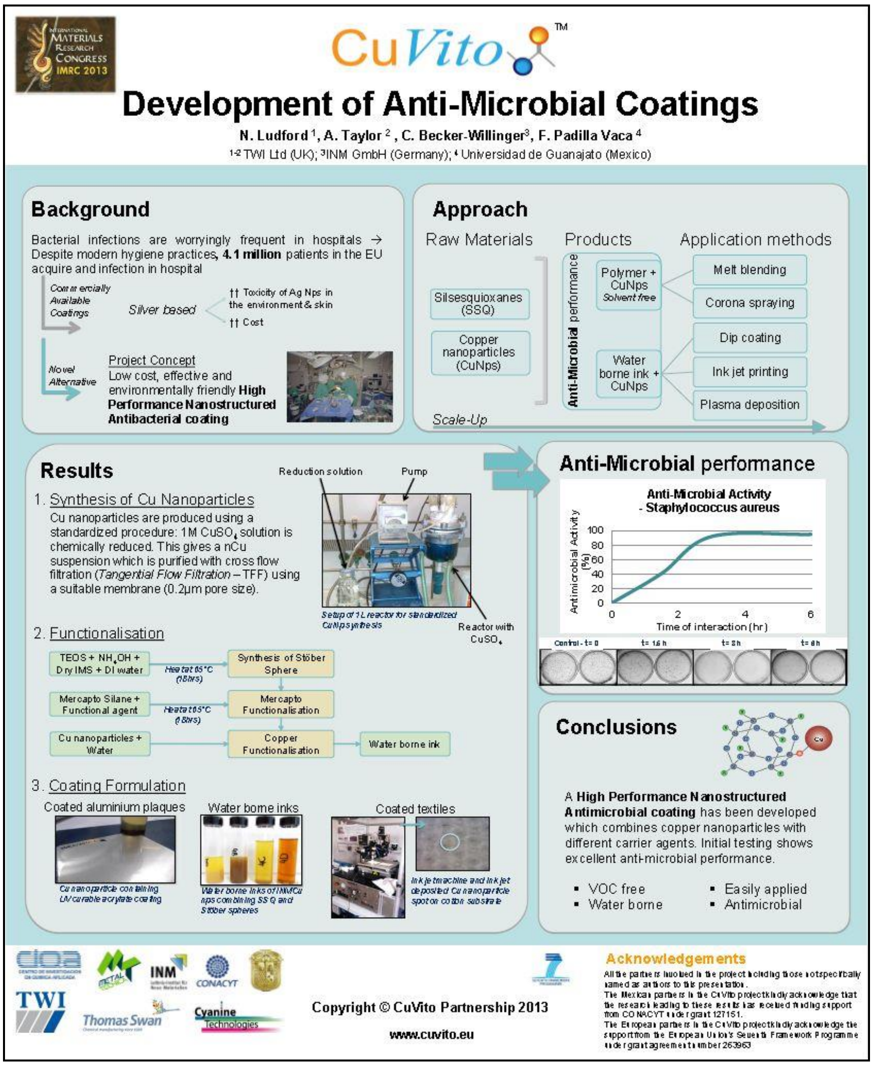

Figure 15 CuVito poster presented at IMRC 2013

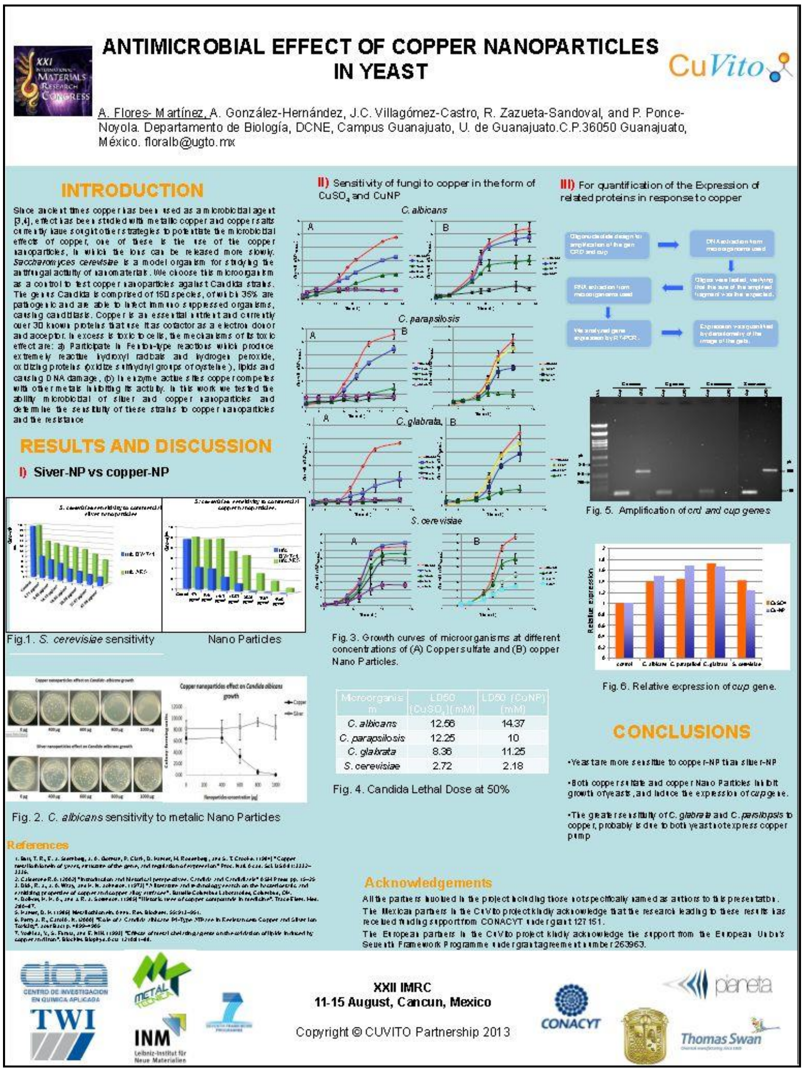

Figure 16 CuVito™ poster presented at IMRC 2012

As well undertaking dissemination activities through attendance at conferences, the project partners also sought to disseminate project results to their commercial partners through normal business activities and discussions. This included the dissemination of project results through appropriate mailing lists etc... TWI hosted a project review and dissemination day at its headquarters in Cambridge during which it was possible to describe the CuVito™ project to MEP Vicky Ford, see Figure 17.

Figure 17 Project co-ordinator Dr Nick Ludford describing the CuVito™ project to MEP Vicky Ford

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