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(71) Applicant: **ECOTICKET, LDA** [PT/PT]; Rua do Conhecimento, n°10, Braga, 4730-575 Soutelo, WD (PT).

(72) Inventor: **NAYOLOR DA ROCHA GOMES, Jaime Isidoro**; Rua do Conhecimento, n°10, Braga, 4730-575 Soutelo, WD (PT).

(74) Agent: **PEREIRA DA CRUZ, João**; J.Pereira da Cruz, S.A., Rua Vitor Cordon, 14, 1249-103 Lisboa (PT).

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(54) **Title**: COMPOUNDS AND REACTIVE NANOPARTICLES OP SILICA WITH INSECT REPELLENT ACTIVITY ON TEXTILE SUBSTRATE AND OTHER MATERIALS AND RESPECTIVE PROCESS OF PREPARATION AND BINDING

(57) **Abstract**: The present invention consists of compounds and reactive nanoparticles with insect repellent activity on textile substrates and other materials and respective process of preparation and binding hydrolysable silanes through a process in which ethyl 3 (N-n-butyl-N-acetylamine) propionate is added to a hydrolysable silane to form a compound that can be bound chemically to fibres or other functional materials. To the product resulting from this reaction a solution of silicate and triton can be added in a sol-gel process, to form reactive silica nanoparticles containing the ethyl 3 (N-n-butyl-N-acetylamine) propionate that are precipitated by lowering the pH. The active product is therefore preferentially but not exclusively included in silica nanoparticles. These nanoparticles have reactive groups that bind by covalent bonds to cellulosic fibres.

DESCRIPTION

"COMPOUNDS AND REACTIVE NANOPARTICLES OF SILICA WITH INSECT REPELLENT ACTIVITY ON TEXTILE SUBSTRATE AND OTHER MATERIALS AND RESPECTIVE PROCESS OF PREPARATION AND BINDING"

FIELD OF THE INVENTION

The present invention consists of compounds and reactive nanoparticles of silica with repellent of mosquitos and other insects, with hydrolysable silane on different surfaces, namely textile substrates. More specifically in a formulation on insect repellent that have amino or hydroxylic in their composition, such as ethyl 3(N-n-butyl-N-acetylamine) propionate with an identical formula to the amino acid alanine, a well known anti-insect, together with an hydrolysable silane that can be applied on substrates such as textiles, paper, leather, paints, varnishes, polymer and other surfaces. The formulation is peferentially incorporated on sílica nanoparticles that are next bound on textile surfaces or others, and preferably nanoparticles with reactive groups that bind by covalent bonds to cellulosic fibres.

Background of the invention

It is well known that insect bites and other parasites can cause itching and rashes. However, some insects such as mosquitos, can transmit viral infections, for example Malaria or Dengue that can cause death to the infected human being. Since it has been verified that insects are present in every season (from winter to summer) it has been realized for several years the necessity to present repellent solutions.

Insect repellents consist in preparations used to repel these insects so as to avoid stings that cause the infection of the skin, forcing them to move away from the human being. The preparations are in the form of lotions, sticks, gel, roll-on, emulsions, sprays, amongst others.

One example of a repellent is DEET (N,N-Diethyl-meta-toluamide) that is used against mosquitos, flies, mite and fleas. However this product is questionable since in the long term it is not known what effect it will have on health.

Another repellent is the ethyl 3(N-n-butyl-N-acetylamine) propionate) with the commercial name IR3535 (Merck) that, sprayed, is very efficient against mosquitos,

ticks and tse-tse flies, amongst others, and Picaridin (Icaridin) with the commercial name Bayrepel (Bayer), also a very efficient mosquito repellent, that are products considered safe for application on the skin. IR3535 for example. It is considered a bio-insecticide by the WHO, World Health Organization since it is an isomer of alanine, an amino-acid.

However, it is verified that even though there are solutions that can be applied on the skin by spray or lotion, the efficiency of these products has been decreasing throughout the years since they have created resistance to the active substances. Besides this disadvantage, the product has to be applied at high concentration, several times a day. For this reason, solutions have emerged that have as objective to increase the efficiency of the performance of the repellents, such as their incorporation in textile fibres. This solution has spurned the developing of some techniques of incorporation and use of some solutions that are going to be presented next.

There are products of high interest for the human health such as insect repellents and insecticides. So as to bind some insect repellents, namely antimosquitos, to textile fibres, such as permethrin and DEET, microencapsulation can be used since in the solid form (microcapsules) it is possible to bind with binding agents.

The products themselves, permethrin and DEET, are liquid products that because they are liquids they dn-thave consistency and it is not possible to fix them onto the fibres, and are applied to fibres in another form, such as mixed with polymeric and dried on top of the fibres, do not resist to more than one or two domestic washes. They might be useful for technical textiles but not for garments (that imply a high number of washes).

The patent application US2010/0183690 refers the microencapsulation of permethrin and demonstrates the application on garment, promoting its durability. Microcapsules with permethrin or DEET, contain normally an essential oil that is a mosquito repellent, such as citronella and eucalyptus. Just as the essential oils permethrin and DEET are products that are totally immiscible in water, but miscible with oils and organic solvents.

Another way of obtaining textiles with additional properties is the immobilization through incorporation with polymeric binders that are applied on the surface of fibres, as described on the document of the US6015570 patent. This document refers one application of insect repellent based on DEET, using binders of silicone.

As an alternative to the products identified, that eliminate or repels insects, we present a new composition

based on the product with the commercial designation of IR3535 from Merck (ethyl 3(N-n-butyl-N-acetylamine) propionate associated to an hydrolysable silane and incorporated on the textile fibres in a way that its efficiency is high after multiple washes. Even though it is used on creams and sprays on the direct application, IR3535 cannot be used in microcapsules since it is a product partially miscible with water. Therefore, a new composition is presented that binds ethyl 3(N-n-butyl-N-acetylamine) propionate to surfaces such as, for example, textile materials that even after multiple washes, a high repellent efficiency is obtained.

It was also detected in this invention that ethyl 3(N-n-butyl-N-acetylamine) propionate is also an activator of the optical brightener Blankphor R, it means that besides being used in this function of the intensification of the effect of the optical brightener, its presence can be detected through this effect. This is an advantage relatively to other repellent products that can only be detected by their effect on mosquitos, that are normally exhaustive tests and take a long time.

On the other hand, patent US2007/0079447 describes a preparation of ethyl 3(N-n-butyl-N-acetylamine) propionate impregnated on textile fibres. A simple impregnation of this product implies that the product be removed straight after

the first washing, since it is not bound by any fixing agent.

For a minimum activity, it would be necessary to incorporate a great quantity of the product so that some of that product would remain after some washes. The waste is huge and the efficiency very small.

Another way is the immobilization through the reacting with the fibres or by the incorporation in polymeric binders that make up the fibres, both processes conveying a bigger washfastness than the microencapsulation that is applied on the surface of fibres as is described in in patent US6015570 and US007&0079447 in which an application of a repellent based on DEET and using binders is described.

There are also antimicrobial products that it is claimed that bind by reaction with the fibre, through a silane group, such as is the case of the product from Aegis (Microban), an antimicrobial cationic agent, even though doubts subsist as for its form of binding, since silane is a group that hydrolyses easily in the presence of water, in the storing or even in the application, not being able after hydrolysis to react with the hydroxy groups of cellulose, as it is claimed. The most probable is a post polymerization with the formation of a film, which is also claimed by the

supplier avoid this type of problem, we propose in our patent, the immobilization of the cationic silane antimicrobial first on the silica nanoparticles that have reactive groups capable of reacting with the fibre and thus they can bind the antimicrobial on fibres without the risk of polymerizing by hydrolysis, since they are already bound to the nanoparticles.

In the case of the insect repellent with groups capable of forming a bond with a coupling agent, as is the case of ethyl 3(N-n-butyl-N-acetylamine) propionate (IR3535), the silane used to bind the nanoparticles is GLYMO, a silane that is stopped from polymerizing because it is bound to the silica nanoparticles, and a silane that does not need a hydrolysable fixing agent, since it contains an epoxy group that reacts with the fibres.

Another form of modifying the textile surfaces of textile surfaces is through a hydrolysable silane such a trimethoxysilane. Sol-gel is a matrix of a metal oxide such as titanium dioxide that forms spontaneously in aqueous medium in the presence of a surfactant, by hydrolysis of a substituent group, such as TEOS, tetraethylorthosilicate, and further polymerization by acid catalysis to form a matrix of silicon oxide.

We may add that the process of preparation of sol-gel is normally done in aqueous medium, so if the is

precursor is hydrophilic, such as silicate, the incorporation of a product is by direct dissolution in water, if it is hydrophobic or immiscible in water, such as TEOS, it should be previously mixed with ethanol to be miscible in water. Taking as an example the silicon oxide sol-gel, the first phase of the formation is the hydrolysis, normally an acid hydrolysis, the silicon precursor for the formation of silicon oxide.

With the continued addition of an acid, or an acid salt, such as ammonium chloride, polymerization occurs by condensation of silicon hydroxide, to form a silica matrix of silicon oxide. The polymeric matrix can involve other hydrophilic products in its interior through the formation of hydrogen bonds.

In this way we can use sol-gel with functional products, as long as they are hydrophilic, such as flame retardants, antimicrobial and others.

From sol-gel, nanoparticles of silica can be precipitated, that have the advantage over other metallic oxides for being porous, and being able to incorporate a functional product that was introduced in the sol-gel.

There are many applications of sol-gel on various surfaces, such as metallic, glass and more recently, textile

materials. However, the functionalization of the textile surfaces for the incorporation of functional products in the sol-gel is still scarce and the incorporation of hydrophobic products and of low solubility in water is a matter that is still under study.

Recently, processes for the development of binding hydrolysable silane films formed on fibres after application through their incorporation in sol-gel of an antimicrobial product (CHT). However it is difficult to control the hydrolysis for the formation of the silane film. It can be formed during the storage of the product such as is mentioned in patent US2009074971.

We may add that the most relevant documents were considered, such as Sol-Gel technology for ecological dyeing of cellulosic fibres and the patent US20070292464. Even though in Sol-Gel Technology for ecological dyeing of cellulosic fibres nanoparticles of silica were mentioned, they do not contain ethyl 3(N-n-butyl-N-acetylamine) propionate and in US20070292464 the microcapsules that contain the insect repellent, ethyl 3(N-n-butyl-N-acetylamine) propionate is encapsulated whereas in the present invention, the binding to the textile fibres of the compound resulting from the ethyl 3(N-n-butyl-N-acetylamine) propionate and the hydrolysable silane that is incorporated in the nanoparticles, is done through a covalent bond, which

itself has a surprising technical effect when compared to the known state of the art since it is guaranteed a high washfastness, an effect that is obtained through the technical differentiating characterristic of the present invention, i.e. the existence of a covalent bond between the compound that contains the active product and the cellulosic fibres.

Summary of the Invention

So as to avoid this type of problem, it is proposed in this patent the immobilization on silica nanoparticles of an insect repellent with groups capable of forming the bond with the coupling agent silane, as is the case of ethyl 3(N-n-butyl-N-acetylamine) propionate (IR3535).

The process includes the formation from the sol-gel of nanoparticles and their precipitation for the formation of a dispersion of nanoparticles that contain the active product. The nanoparticles are then bound to the textile material through a reactive group present in the nanoparticles. To obtain this result it is necessary to previously functionalize the nanoparticles that contain the active product with an appropriate group for reaction with the cellulosic fibres, such as the epoxy group, so as to fix them afterwards on the textile material.

There are products with epoxy groups, immobilized directly in textile fibres, such as products of cationization of cotton, GLYTAC and CTHAC. Their bond is through the epoxy group that reacts with the fibres in alkaline medium. There aren't any solutions for binding in which the product is bound to the textile fibres through reactive silica nanoparticles. The solution we propose in particular in this patent, is the immobilization of the active product on the silica nanoparticle through a compound that contains an epoxy group, or other group known for reacting with cellulosic fibres from a non-exclusive list that is shown below:

-vinylsulphone
-florochloropyrimidine
-dichlorotriazine
-monochlorotriazine
-aziridine
-bromochloropirimidine
-florotriazine

The active product, after forming a compound with the epoxysilane, can bind to cellulosic fibres through the reaction with an epoxy group guaranteeing in this way a high washfastness because of an existing covalent bond between

the compound containing the active product and the cellulosic fibres.

Detailed description of the Invention

The ethyl 3(N-n-butyl-N-acetylamine) propionate (IR3535), is a product known for the efficiency in insect repellency, more specifically mosquitos. In chemical terms, the ethyl 3(N-n-butyl-N-acetylamine) propionate is characterized by being majorly hydrophobic. This property makes its incorporation in microcapsules, difficult, since this is a product that is partially miscible with water, microencapsulation wouldn't be viable in an oil in water emulsion (o/w), it would mean that one part would remain in water and therefore out of the microcapsule. In the case of microcapsules there is also the issue of the limitation in the number of washes they resist, since they burst during the washes, due to friction and lose their functional content during the process of washing.

The present invention consists in a formulation of insect repellents or antimicrobial that are immiscible in water or almost totally immiscible in water, with hydrolysable silanesand nanoparticles of silica, and that contain amino groups and/or hydroxyl groups capable of forming hydrogen bonds with a silica matrix of a sol-gel, and that after being applied in this form, or in the form of

nanoparticles of silica to a textile substrate, a strong bonding on the textile fibres is obtained on the textile fibres and a corresponding high efficiency even after multiple washes, via the reactive groups also incorporated during the sol-gel process.

Taking that into consideration, and so as to prepare a formulation that allows the bonding of ethyl 3(N-n-butyl-N-acetylamine) propionate to a substrate such as for example a textile, it is necessary to add an epoxysilane coupling agent such as 3-glycidylpropylmethoxysilane (GLYMO). 3-glycidylpropylmethoxysilane is made up of a glycidyl group that transforms into epoxy in alkaline or neutral conditions, and a silane group. When adding 3-glycidylpropylmethoxysilane GLYMO to the ethyl 3(N-n-butyl-N-acetylamine) propionate the silane group reacts with the amino group.

Since the reaction of the silane group with amino acids as for example enzymes is known, and since ethyl 3(N-n-butyl-N-acetylamine) propionate is the amino acid alanine, the reaction with 3-glycidylpropylmethoxysilane forms a covalent bond. The epoxy group of 3-glycidylpropylmethoxysilane will be available to bond to the substrate that is going to be used. In case the substrate is textile, and the application is a direct application, the epoxy reacts with the hydroxyl groups of cellulosic fibres

or other fibres and materials containing hydroxyl groups or other nucleophilic groups such as amine NR2, where R is a hydrogen or radical such as methyl, ethyl, propyl, butyl, etc.

Gel formation

Generally, if the product that is going to be incorporated is hydrophilic, the silica precursor is also hydrophilic and the incorporation of the product is by direct dissolution in water. This is the case for sodium silicate. In the present invention, the sol-gel is modified. Since the active product is mostly immiscible in water, ethyl 3(N-n-butyl-N-acetylamine) propionate is firstly made to react with an hydrolysable silane, a sol-gel of an oil in water emulsion (o/w) is prepared by adding a silica precursor in aqueous phase, sodium silicate or TEOS, the latter one previously mixed with ethanol. One advantage is it being an aqueous medium process, it avoids solvent and turning it into a more ecological process.

Another advantage as referred previously is the fact of it being possible to use a hydrolysable silane such as 3-glycidylpropylmethoxysilane to bind the ethyl 3(N-n-butyl-N-acetylamine) propionate to the silica nanoparticles which stops the silane of polymerizing when binding the product through a silane group to the cellulosic fibres,

since the molecule is already bound to the nanoparticles. In this way it is possible to bind products to fibres and other materials, storing the product in an aqueous medium, without the risk of polymerizing during the storage.

Binding via silica nanoparticles

From the sol-gel, the silica nanoparticles are precipitated adding more acid at the end of the process of formation of the sol-gel, with mixing, forming in this way a bond of the ethyl 3(N-n-butyl-N-acetylamine) propionate with the silica nanoparticles, by means of a bond between the silane and the silicon group of the silica. A dispersion of the nanoparticles is applied to the material, binding the nanoparticles containing the ethyl 3(N-n-butyl-N-acetylamine) propionate during the process of thermofixation with the aid of a coupling agent such as an hydrolysable silane, by a process known to the industry of textile finishing as Pad-fix, which consists of a passage of the textile material through a tank containing the products followed by a continuous thermofixation process in an equipment designated by stenter.

In the case of cellulosic or proteic fibres, and the hydrolysable silane having an epoxy group, such as GLYMO-glycidylpropyltrimethoxysilane for example, the nanoparticles can be bound to the fibres through the epoxy

group already bound to the nanoparticles, without the necessity of the addition of a binder or another reactive group. The process of reaction between the epoxy of the nanoparticles and the cellulosic fibres, or proteic fibres, is promoted by temperature and alkaline pH.

In the present invention for the product that includes ethyl 3(N-n-butyl-N-acetylamine) propionate to have a durability superior to the number of washes of textile articles, it needs to be bound to the cellulosic fibres through the glycidyl CH_2CH_2OH groups, that after forming the epoxy ring in alkaline conditions it reacts with the cellulose, the functional products or 3(N-n-butyl-N-acetylamine) propionate therefore staying bound to the fibre, the glycidyl group in its epoxy form of GLYMO acting as a linker (coupling agent) between these compounds of insect repellency to the cellulosic fibres.

In the present invention we claim a product that is formed by the reaction of ethyl 3(N-n-butyl-N-acetylamine) propionate (3) with an hydrolysable silane containing an epoxy group and one other group of hydrolysable silane, such as GLYMO, but not exclusively, a product being formed in this way that is part of the sol-gel, formed during the process described above, through chemical bonds and that in turn bonds to cellulosic fibres through the epoxy group in GLYMO, after a process of thermofixation onto the textile

material. As a previous formation of the nanoparticles has already taken place from the sol-gel, and since the product is bonded to the nanoparticles through the silane group, and as the silane compound contains epoxy, these will bind the nanoparticles to the fibres.

Application of the product without nanoparticles

As an alternative, functional products can be bound directly to the fibres through GLYMO, in which the reaction of ethyl 3(N-n-butyl-N-acetylamine) propionate occurs in loco when of the application on the material. The product of the reaction between ethyl 3(N-n-butyl-N-acetylamine) propionate with the trimethoxysilane of GLYMO can also be prepared previously and apply it later to the textile material. The compound is bound through the epoxy group in the absence of water to avoid hydrolysis.

Application to other materials

In the case of paper it can be by spray or in the process of production of the paper itself, incorporating the nanoparticles with the ethyl 3(N-n-butyl-N-acetylamine) propionate in the paper pulp. In the case of packages made of paper it can be by printing or coating, in the case of construction surfaces such as walls and floor, or other materials that are coated by paints or varnishes, it can be

by coating just as pains and varnishes are applied, it being possible for the products that result from the reaction of the ethyl 3(N-n-butyl-N-acetylamine) propionate with the hydrolysable silane, incorporated or not in the nanoparticles, to be mixed in the paint itself or the varnish.

For the binding to these materials, the material should be heated at temperatures that promote the polymerization of the hydrolysable silane such as is already done for the application of sol-gel containing hydrolysable silanes. In other materials such as polymers, it can be by coating or spray, or incorporated during the production of the polymer. In this case, because the aqueous medium cannot be used, the silica nanoparticles containing the ethyl 3(N-n-butyl-N-acetylamine) propionate themselves are incorporated.

Object of the invention

A preferential object of this invention is products resultant from the reaction between ethyl 3(N-n-butyl-N-acetylamine) propionate and a hydrolysable silane without resorting to nanoparticles and in the absence of water.

It is a preferential object of this invention the preparation of the reactive nanoparticles that consists of the following steps:

a) The addition of ethyl 3(N-n-butyl-N-acetylamine) propionate to a hydrolysable silane, The mixture that is stirred and left to react for 2 hours at a temperature between 10 and 60°C.

b) The addition of the product resulting from the reaction of step a) to a solution of sodium silicate and of a tensoactive

c) Stirring for 60 minutes and after this period acetic acid is added until a neutral pH is obtained for the formation of the sol-gel.

d) The addition of ammonium chloride until the pH lowers until 4 forming the nanoparticles and causing their precipitation.

e) Drying after which the nanoparticles of silica are obtained.

It is a preferential object of this invention a binding process of the reactive nanoparticles of silica

antimosquito on materials such as fibres, paints, varnishes, metals, paper, leather, wood.

Preferentially the binding of the nanoparticles to textile fibres is obtained through the epoxy group.

In a preferential way of binding of the reactive nanoparticles to textile fibres, they are applied:

a) In an aqueous dispersion by a process of Pad-Fix at an alkaline pH and at a temperature of fixation (binding) of 130°C; or

b) In by exhaustion in a rotating piece dyeing machine on garments at an alkaline pH and a temperature of 40°C followed by a thermofixation in a tumbler dryer; or

c) manually by impregnating the fibres in an aqueous dispersion of nanoparticles in which the pH is adjusted to 9 leaving it soaking for a period of 30 minutes, followed by drying in air or in the sun at a temperature above 30°C

Preferentially the binding of the reactive nanoparticles to paper is carried out by:

a) Spray; or

b) When producing the paper incorporating the nanoparticles with the ethyl 3(N-n-butyl-N-acetylamine) propionate in the paper pulp; or

c) Printing.

In a general way the process of binding the reactive silica nanoparticles on surfaces such as floor, walls, paints, varnishes, being by:

a) Coating in which the product resultant from the reaction of the ethyl 3(N-n-butyl-N-acetylamine) propionate and the hydrolysable silane, incorporated or not in the nanoparticles, being mixed in the paint or the varnish.

b) Spray.

The invention is illustrated by the following Examples that do not represent in any way a limitation.

EXAMPLES

Example 1 - Preparation of reactive nanoparticles

2 ml of ethyl 3(N-n-butyl-N-acetylamine) propionate are added to 2ml of GLYMO and it is stirred during and reacts

during 2 hours at a temperature between 10 and 60°C. The product resulting from this reaction is added to 200 ml of a solution of silicate and 2g/l of triton. After 60 minutes of stirring, acetic acid is added until the pH lowers down to 4 for the formation of nanoparticles and their precipitation. After drying it is observed that 4 g of silica nanoparticles are obtained.

Example 2 - Application on textile materials by impregnation via a Pad-Fix process, of reactive antimosquito nanoparticles.

A woven 100% cellulosic fabric of 200 g/m2 of weight was padded in a pad-mangle constituted of an immersion tank and two squeeze rollers, with a mixture made up of 50 g/l reactive nanoparticles of silica containing ethyl 3(N-n-butyl-N-acetylamine) propionate, in one liter of water. The pH was adjusted to 9 and 10 g/l was added with a dispersing agent. It was then subjected to thermofixation in a stenter at a temperature of 130°C for a period of 5 minutes.

Example 3 - Application on textile materials by exhaustion with reactive antimosquito nanoparticles

One batch of 100 T-shirts of 100% was added to an aqueous dispersion of reactive silica nanoparticles containing ethyl 3(N-n-butyl-N-acetylamine) propionate at an

alkaline pH of 9 and a temperature of 40°C, in a rotating drum machine for 30 minutes. It was then centrifuged and then dried above 100°C in a drying tumbler machine, where thermofixation occurs on the textile material (T-shirt).

Example 4- Application of antimosquito formulation with reactive groups

To a 100% cotton woven fabric, in a pad-mangle a mixture previously prepared made up of 100 g/l of ethyl 3(N-n-butyl-N-acetylamine) propionate and GLYMO (1:1) in water , followed by a thermofixation in a stenter at 130°C, all the process being continuous at a speed of 10 m/min.

Process for the measurement of IR3535 ethyl 3(N-n-butyl-N-acetylamine) propionate in a textile article

Optical brightener: absorbs in the visible and emits in the uv, conveying a whiter hue to the fibres.

To determine the presence of IR3535 on the textile fibres a colorimetric method conjugating the reaction of IR3535 with both products, silane and Blankophor R, a product that reflects in the wavelength of 440 nm.

CLAIMS

1. Compound resulting from the reaction of ethyl 3(N-n-butyl-N-acetylamine) propionate and a hydrolysable silane.

2. Compound with insect repellency activity according to claim 1 a wherein the hydrolysable silane group has the formula (RO)3Si- in which R is a radical of general formula C_2H_{2n+1}

3. Compound with insect repellency activity according to claim 1, wherein the silane contains an epoxy group.

4. Reactive nanoparticles of silica with insect repellency activity, according to claim 4, characterized by containing the product of claim 1.

5. Reactive nanoparticles of silica with insect repellency activity, according to claim 4, wherein the ethyl 3(N-n-butyl-N-acetylamine) propionate is immobilized through the bond with a silane.

6. Reactive nanoparticles of silica with insect repellency activity, according to claim 4, wherein the nanoparticles are fixd (bound) on materials such as fibres, paints, varnishes, metals, paper, leather, wood.

7. Sol-gel process for preparation of insect repellent reactive silica nanoparticles consisting of the following steps:

a) The addition of ethyl 3(N-n-butyl-N-acetylamine) propionate to a hydrolysable silane, The mixture that is stirred and left to react for 2 hours at a temperature between 10 and 60°C.

b) The addition of the product resulting from the reaction of step a) to a solution of sodium silicate and of a tensoactive.

c) Stirring for 60 minutes and after this period acetic acid is added until a neutral pH is obtained for the formation of the sol-gel.

d) The addition of ammonium chloride until the pH lowers until 4 forming the nanoparticles and causing their precipitation.

e) Drying after which the nanoparticles of silica are obtained.

8. Sol-Gel process for preparing insect repellent reactive silica nanoparticles according to claim 7, wherein the product resultant from the reaction of step a) is immiscible in water or almost totally immiscible in water.

9. Process of binding the products of claims 1 and 2 on materials such as textile fibres, paints, varnishes, paper, leather, wood, characterized by the nanoparticles being applied on the textile fibre:

a) In an aqueous dispersion by a Pad-fix process at an alkaline pH and at a fixation temperature of 130°C; or

b) by exhaustion in a rotating tumbler machine on already made garments at an alkaline pH at a temperature of 40°C followed by a thermofixation process by drying in a tumbler; or

c) manually by impregnating the fibres in an aqueous dispersion of nanoparticles in which the pH is adjusted to 9 leaving it soaking for a

period of 30 minutes, followed by drying in air or in the sun at a temperature above 30°C.

10. Process of binding of the reactive silica nanoparticles according to claim 9 wherein a hydrolysable silane as a coupling agent between the nanoparticles and the fibre.

11. Process of fixation of the reactive silica nanoparticles according to claim 10 wherein the hydrolysable silane is 3-glycidylpropyltrimethoxysilane.

12. Process of fixation of the reactive silica nanoparticles according to claim 9 wherein the fixation (binding) of the nanoparticles to the fibres is through an epoxy group.

13. Process of fixation of the nanoparticles according to claim 9 wherein the binding to paper is carried out by:

a) Spray; or

b) When producing the paper incorporating the nanoparticles with the ethyl 3(N-n-butyl-N-acetylamine) propionate in the paper pulp; or

b) Printing.

14. Process of binding the reactive silica nanoparticles according to claim 9 characterized by the binding on surfaces such as floor, walls, paints, varnishes, being by:

a) Coating in which the product resultant from the reaction of the ethyl 3(N-n-butyl-N-acetylamine) propionate and the hydrolysable silane, incorporated or not in the nanoparticles, being mixed in the paint or the varnish; or

b) Spray.

INTERNATIONAL SEARCH REPORT

International application No
PCT/PT2014/000041

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N37/46 A01N55/10 A01P17/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, BIOSIS, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/120440 A1 (MERCK PATENT GMBH [DE]; WALENZYK THOMAS [DE]; CAROLA CHRISTOPHE [DE];) 22 December 2005 (2005-12-22) page 3, paragraph 2 claims 1-3,7,11-15,27 examples 1-5	1-14
A	US 2003/165452 A1 (GONZALEZ ANTHONY D [US] ET AL) 4 September 2003 (2003-09-04) paragraph [0018]	1-8
A	US 2007/292464 A1 (MATHIS RAYMOND [DE] ET AL) 20 December 2007 (2007-12-20) cited in the application claims 1-19	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 2014	01/10/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marie, Gérald

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/PT2014/000041

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005120440 A1	22-12-2005	AT 452620 T	15-01-2010
		EP 1763383 A1	21-03-2007
		US 2008260664 A1	23-10-2008
		WO 2005120440 A1	22-12-2005
US 2003165452 A1	04-09-2003	NONE	
US 2007292464 A1	20-12-2007	DE 102006016907 A1	25-10-2007
		EP 1845186 A1	17-10-2007
		JP 5484656 B2	07-05-2014
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		US 2007292464 A1	20-12-2007