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(54) Title: AN ANTIMICROBIAL FOOD PACKAGE

(57) Abstract: A package comprising packaging material defining an enclosed space suitable for containing an item susceptible to microbial growth or spoilage is described. An interior of the package comprises at least one antimicrobial surface bearing an ordered nanoarray of metal or metal oxide nanostructures. A packaging material in the form of a sheet or film having a first face and a second face, in which at least a portion of one of the first or second faces of the film comprises a surface bearing a nanoarray of metal or metal oxide nanostructures, is also described.

Title

An antimicrobial food package

Introduction

5 The invention relates to an antimicrobial package suitable for containing an item susceptible to microbial growth or spoilage. In particular, the invention relates to an antimicrobial package for comestible products such as food and drink products.

10 Microbial contamination of food reduces the quality of food, limits the shelf-life of the food, and increases the risk of food-borne illness to the consumer. Contamination occurs primarily on the surface of foods, especially foods such as cheeses and meats. For the food industry, prevention of food spoilage is an important variable when determining profit. Moreover, prevention of food spoilage can prolong the shelf-life of products and thus extend market boundaries, resulting in increased profit. The growth of microorganisms on food products
15 largely occurs post processing during stroage, therefore the packaging of the ffod is extremely important to the quality and shelf life of the food.

The antimicrobial properties of silver have been recognised for a long time. More recently, silver nanoparticles have been recognised as having antimicrobial properties, and have been
20 suggested for use as an antibacterial agent in surgical masks, wound dressings, and cotton fibres, Use in food packaging has also been described – see for exampl Appendini et al, Innovative Food Science & Emerging technologies, 2002, Vol. 3, US6942897, US10/726512, WO2004/012998, and US7311933. Use in food packaging, where silver-containing nanoparticles are incorporated into the matrix of polymeric packaging materials,
25 has not gained acceptance due to percieved health risks associated with the silver nanoparticles, and also due to the large amounts of metal required to achieve an antibacterial effect (1-5wt%).

EP1932429 describes a food package on a cellulose hydrate base that contains nano-scale
30 additives. The involved nano particles measure from 0.5 to 1000 nm in at least one dimension. The nano particles can be evenly distributed in the cellulose hydrate matrix, they can be on the surface or they can be concentrated in near-surface areas. The invention also contains a procedure for the production of the food package and its use as an artificial sausage skin.

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DE102007044286 concerns a transport container, especially for the transport of food. The container is made up of polymeric foam with an anti-bacterial active substance. The invention also describes the methodology of the process of manufacturing the food package.

5 EP1972197 describes a procedure for the manufacture of a food package with anti-microbial properties, in which nano-silver is applied to the outer side of the food package or worked into a food package by means of application to various types of varnishes or adhesives. This invention also concerns a food package with antimicrobial properties as well as the use of such a container to package (envelope) food.

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The methods described in the three patent documents above all involve an initial step of synthesising nanoparticles as an initial step, and then incorporation of the formed nanoparticles into a polymer to provide an active surface. The step of pre-forming, and subsequent handling, of nanoparticles involves significant toxicological challenge. In addition, the processes involve use of significant amounts of nanoparticles (1-5%).

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It is an object of the invention to overcome at least one of the above-referenced problems.

Statements of Invention

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The Applicant has solved the above-referenced problem by the provision of a package defining an enclosed space suitable for containing an item, in which an interior of the package comprises a surface bearing an ordered nanopattern or nanoarray of metal or metal oxide nanostructures.

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The term “ordered nanopattern or nanoarray of metal or metal oxide nanostructures” should be understood to mean an arrangement of metal or metal oxide structures, for example nanodots or nanolines, that are formed on a surface of a substrate in an equispaced pattern, have dimensions in a nanometre range, and are formed by self-assembly from a microphase separated block copolymer in which one of the polymers selectively incorporates a metal ion salt prior to treatment of the block copolymer to oxidise the metal ion salt and remove the polymers. Methods of forming such arrays or patterns of nanostructures is described in the semi-conductor and microelectronics literature, albeit not in the context of antimicrobial packaging - see for example: US2010/102415; Kuemmel et al., J. Sol Gel Sci. technol. 2008, Vol. 48; CN101609743; and US2011/250745. The invention therefore relates to the use of a

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surface bearing such an ordered nanopattern or nanoarray of metal or metal oxide nanostructures as an antimicrobial surface in a packaging for an item prone to microbiological spoilage or growth.

Thus, the invention provides a package for an item, typically an item susceptible to microbial growth or spoilage, ideally a comestible product, in which an interior of the package comprises a surface that bears a nanoarray or nanopattern of metal or metal oxide nanostructures.

A packaging material according to the invention, overcomes a number of problems of the prior art. First, as the process for making the product does not involve an initial step of forming nanoparticles, the toxicological risks associated with the methods of EP1932429, DE102007044286, and EP19721297 are obviated. Second, the provision of an ordered nanoarray of nanostructures, for example nanostructures of silver oxide, significantly reduces the amount of silver required to achieve an antimicrobial effect ($<0.001\text{wt}\%$) compared to convention technology where silver-containing nanoparticles are incorporated into the packaging material at 1-5wt%. Further, due to their process of manufacture, the nanostructures are rigidly anchored to the surface on which they are formed, thereby allaying concerns that the nanostructures will be ingested by consumers.

The invention also provides a package defining an enclosed space containing an item, generally an item susceptible to microbial growth or spoilage, in which an interior of the package comprises a surface bearing a nanopattern or nanoarray of metal or metal oxide nanostructures.

The invention also relates to a packaging material in the form of a sheet or film, for example a roll of polymeric film, having a first face and a second face, in which at least a portion of one of the faces of the film comprises a surface bearing a nanopattern or nanoarray of metal or metal oxide nanostructures.

The invention also relates to the use of a packaging material of the invention as an antimicrobial agent, typically an antimicrobial agent against packaged comestible items such as food products.

The invention also relates to a method of extending the shelf life of a packaged comestible item, typically a food product, which method employs a packaging material at least part of which comprises a surface bearing a nanoarray of metal or metal oxide nanostructures, the method comprising a step of enclosing the comestible item within the packaging material to form a package such that the surface bearing the nanoarray of metal or metal oxide nanostructures is disposed on an interior of the package. The surface bearing the nanoarray of

metal or metal oxide nanostructures may be integrally formed with the packaging material, or may take the form of an insert.

5 The invention also relates to a method of preserving a packaged comestible item, typically a packaged food product, which method employs a packaging material at least part of which comprises a surface bearing a nanoarray of metal or metal oxide nanostructures, the method comprising a step of enclosing the comestible item within the packaging material to form a package such that the surface bearing the nanoarray of metal or metal oxide nanostructures is disposed on an interior of the package. The surface bearing the nanoarray of metal or metal
10 oxide nanostructures may be integrally formed with the packaging material, or may take the form of an insert.

The invention also relates to a method of preventing or inhibiting microbial growth on a comestible item contained within a package, typically a packaged food product, which
15 method employs a packaging material at least part of which comprises a surface bearing a nanoarray of metal or metal oxide nanostructures, the method comprising a step of enclosing the comestible item within the packaging material to form a package such that the surface bearing the nanoarray of metal or metal oxide nanostructures is disposed on an interior of the package. The surface bearing the nanoarray of metal or metal oxide nanostructures may be
20 integrally formed with the packaging material, or may take the form of an insert.

The invention also relates to the use of a substrate having a surface bearing an array of metal or metal oxide nanostructures as a packaging material for an item susceptible to microbial growth or spoilage, especially a comestible item such as a food product. Typically, the
25 substrate is a material suitable for packaging, such as for example a material formed from a polymeric, paper, foil, material or composites thereof.

Detailed Description of the Invention

30 Methods for generating a nanoarray of metal or metal oxide nanostructures on a substrate are known from the literature in the field of microelectronics, and are described in many of the documents as a resist for pattern transfer to a substrate via an etch process. The invention is based on the finding that such nanoarrays have antimicrobial properties, and may be provided on packaging materials to confer an antimicrobial property to the packaging material. Items
35 that are packaged in such packaging material are therefore subjected to the antimicrobial effects of the nanoarray of nanostructures. The invention is particularly applicable to the packaging of comestible items that are susceptible to microbial growth or spoilage.

The metals employed for the package, packaging materials, and methods and uses of the invention, may be selected from the group consisting of:

- 5 The surface bearing the nanoarray or nanopattern of nanostructures may be an interior surface of the packaging material itself, or it may be an insert that it inserted into the package. Inserts could be, for example, a planar film or card on which the nanoarray of nanostructures is formed. The packaging material may be polymeric, for example a polymeric bottle, pouch, tray, wrapper, bag, carton or film, with the nanostructures formed on an interior surface of the material, preferably a portion of the material that in use is in contact with at least a portion of
10 the item.

Typically, the nanoarray or nanopattern of nanostructures has a density on the surface of at least 1×10^6 nanostructures/cm², preferably at least 1×10^7 nanostructures/cm², preferably at
15 least 1×10^8 nanostructures/cm², preferably at least 1×10^9 nanostructures/cm², preferably at least 1×10^{10} nanostructures/cm². The nanostructures generally have a diameter of from 10-50nm, preferably 15-30nm, more preferably 20-30nm. Suitably, the centre to centre distance of the nanostructures is 30-60nm, preferably 40-50nm. Characterisation techniques such as atomic force microscopy, secondary electron microscopy, and helium ion microscopy, are
20 employed.

Typically, the nanostructures have a flattened dome shape, such that the edges of the nanodot are not less than one fifth of the height at the centre. However, other types of nanostructures are envisaged, for example lines.
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In one embodiment, the nanoarray or nanopattern of nanostructures is ordered (i.e. in an eqispaced pattern), and ideally periodically ordered. The term “periodically ordered” should be understood to mean that the system exhibits a pattern formed that has both short range and long range order. In this way the local pattern is reproduced so that the spacing of features is
30 uniform in any chosen direction across the substrate.

The nanoarray of nanostructures may be provided in a pattern, for example having a round, oval, square, rectangular, triangular, or any other shape. Moreover, the surface may bear a plurality of nanoarrays, for example a pattern of dots on the surface in which each dots
35 comprises a nanoarray of nanostructures.

Typically, the metal is a transition metal (i.e. iron, copper, silver, nickel, aluminium, tungsten, silicon cadmium) or a lanthanide (i.e. cerium), although other metals may be employed in the present invention. Preferably, the metal is silver.

5 The term “metal oxide” as employed herein should be understood to mean a chemical compound containing a metal and an anion of oxygen typically in a -2 state. Generally, the metal is selected from a transition metal (i.e. iron, copper, silver, nickel, aluminium, tungsten, silicon cadmium) or a lanthanide (i.e. cerium), although other metals may be employed in the present invention.

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The term “metal ion salt” should be understood to mean an ionic compound comprising a salt-forming metal cation and a salt-forming anion. Examples of salt-forming anions include nitrates, nitrites, phosphates, sulphates, chlorides and carbonates. Suitably, the metal ion salt is a metal nitrate, for example iron (III) nitrate nonahydrate, cerium nitrate hexahydrate, and
15 copper nitrate hemipentahydrate.

The term “item susceptible to microbial growth or spoilage” should be understood to mean an item that supports microbial growth in a packaged environment. Examples of items are comestible products, such as food and drink products, including red meat, poultry, fish,
20 shellfish, vegetables, fruit, ready-made meals, dairy products, yoghurts, yoghurt drinks, fruit drinks, confectionary products.

Various forms of packages may incorporate a surface bearing a nanopattern or nanoarray of metal or metal oxide nanostructures, for example:

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- film packaging, where the item is wrapped in the film and an interior face of the film provides the surface bearing the metal nanostructures – the antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
- film plus tray packaging, where the item sits in a tray and the item and tray are wrapped
30 in a film. In this case, the nanostructures may be formed on the tray, an interior surface of the film, or both, and the antimicrobial surface may extend across all, some or only a portion of the interior face of the film or the tray;
- TETRAPAK packs, generally for drinks, milk, soups, sauces, yoghurts, in which the nanostructures are generally formed on an inner surface of the pack - the antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
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- plastic wrappers, for example wrappers for chocolate bars or plastic wrapping for snacks, where the nanostructures are generally formed on an inner surface of the pack - ; the

antimicrobial surface may extend across all, some or only a portion of the interior face of the film

- plastic bag type packages, such as those employed to pack potatoes and vegetables, where the nanostructures are generally formed on an inner surface of the pack- the antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
- paper or paper polymer composite sheets, of the type employed to wrap fish and which is sealed by heat-sealing, where the nanostructures are generally formed on an inner surface of the sheet - the antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
- plastic bottles or vials, of the type employed to contain beverages or liquid samples, where the nanostructures are generally formed on an inner surface of the bottle, and typically disposed on a part of the inner surface of the bottle that in use is in contact with the item contained within the bottle. The antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
- glass bottles, where the nanostructures are generally formed on an inner surface of the pack - the antimicrobial surface may extend across all, some or only a portion of the interior face of the film;
- cardboard boxes or cartons.

The surface bearing a nanopattern or nanoarray of metal or metal oxide nanostructures may be integral with the packaging material, or may be separate from the packaging material, for example an insert in the form of, for example, a sheet of card or polymer. The insert may be disposed within the package such that in use substantially all or a part of the insert abuts at least a part of the item. The surface bearing the nanopattern or nanoarray is preferably disposed within the packaging such that it abuts the item contained within the package. Thus, substantially all or a portion of the surface bearing the nanoarray of metal or metal oxide nanostructures generally abuts substantially all or a portion of the item contained within the packaging.

The packages of the invention ideally enclose the packaged item, This means that they fully or partially enclose the item.

Nanorrays of metal or metal oxide nanostructures are created from a simple block copolymer self-assembly technique. Briefly, a thin film of a microphase separating solution is applied to a substrate (ceramic, metal, glass, polymer and films thereof) which is then treated by heating and/or solvent exposure to induce microphase separation into an ordered nanopattern. The

so-formed film is then subject to exposure to a solvent containing metal cations. The solvent is chosen so that it selectively swells one block allowing the metal cations to enter one block. The substrate is removed and dried and placed under a UV/ozone atmosphere for a period of time. During this, the metal cations are oxidized to a solid oxide replication the polymer pattern formed by the microphase separation. The remaining polymer material is also oxidized in the treatment to CO₂ so that a surface containing nanodots of metal oxide may be formed. Reduction to metal (from the oxide) can be achieved by exposure to reducing gas. The nanodots formed (oxide or metal) are well-adhered to the surface, robust, thermally stable and of uniform size. Nanodot sizes of 5nm to 100nm in diameter can be formed by choice of block copolymer.

Experimental

Example 1

A polystyrene-b-poly(ethylene oxide) (PS-b-PEO) diblock copolymer was purchased from Polymer Source and used without further purification (number-average molecular weight, M_n , PS = 42 kg mol⁻¹, M_n , PEO = 11.5 kg mol⁻¹, $M_w/M_n = 1.07$, M_w : weight-average molecular weight). Microscopic glass substrates were cleaned by ultrasonication in ethanol and toluene for 30 min each and dried under a nitrogen stream. PS-b-PEO was dissolved in toluene to yield 0.9 wt% polymer solution at room temperature and this solution was aged for 12 hours. The PS-b-PEO thin film was fabricated by spin coating the polymer solution at 3000 rpm for 30 sec on Si wafer. The film was exposed to toluene/water (50:50, v/v) mixed vapour placed at the bottom of a closed vessel kept at 50°C for 1h to induce mobility and allow microphase separation to occur. Separate reservoirs were used for each solvent to avoid azeotropic effects. The resultant phase separated film was immersed in ethanol at 40°C for 15h. For the fabrication of silver and zinc oxide nanodots silver nitrate (AgNO₃) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) were used respectively. 0.6wt% and 1wt% concentrations of silver and zinc precursors were dissolved in ethanol respectively and spin coated onto the nanoporous film. UV/Ozone treatment (3h) was used in order to oxidize the precursor as well as to remove polymer residues. The spin coating of the precursors and UV/Ozone treatment were repeated four times in order to increase the concentrations of the resultant nanodots.

Example 2

A polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) diblock copolymer was purchased from Polymer Source and used without further purification (number-average molecular weight, M_n , PS = 24 kg mol⁻¹, M_n , PEO = 9.5 kg mol⁻¹, $M_w/M_n = 1.06$, M_w : weight-average molecular weight). A polymethylmethacrylate (PMMA) 400 micron thick film was cleaned by

immersion in ethanol and ultrasonicated in the same solvent for 10 min. The film then dried under a nitrogen stream. PS-b-P4VP was dissolved in toluene to yield 0.5 wt% polymer solution at room temperature and was ultrasonicated for 10 min to ensure dispersion of the polymer. The PS-b-P4VP thin film was fabricated by spin coating the polymer solution at 3000 rpm for 30 sec on Si wafer. The film was exposed to toluene vapour placed at the bottom of a closed vessel kept at 50⁰C for 2 h to induce chain mobility and allow microphase separation to occur. The film was immediately removed and placed in a similar arrangement so that the film was exposed to ethanol vapour for 20 min. The sample was removed and placed into ethanol containing 0.5 weight percent silver nitrate at 40⁰C for 15 min. The film was removed and dipped into clean ethanol for around 10 s. this was repeated twice before drying of the film. UV/Ozone treatment (1h) was used in order to oxidize the precursor as well as to remove polymer residues. The spin coating of the precursors and UV/Ozone treatment were repeated four times in order to increase the concentrations of the resultant nanodots.

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Example 3

The same PS-b-P4VP diblock copolymer described in example 2 was used here. A sheet (30 cm x 30 cm) of aluminized polyvinylchloride food was cleaned by exposing to a UV/ozone mixture for 10 min. PS-b-P4VP was dissolved in toluene to yield 0.25 wt% polymer solution at room temperature and was ultrasonicated for 10 min to ensure dispersion of the polymer. The PS-b-P4VP thin film was fabricated by dip coating the sheets into the polymer solution and removing when a knife edge was drawn across the film to remove excess solution. The sheet was exposed to toluene vapour by placing the sheet on a self-supporting gauze support 1 cm above the bottom of a tray containing toluene. The tray was covered and sealed with a steel lid. All solvent treatments were a room temperature for a period of 2 h The sheet was removed and placed in a similar arrangement so that the film was exposed to ethanol vapour for 20 min. The sample was removed and placed into ethanol containing 0.25 weight percent copper nitrate at 20⁰C for 15 min. The film was removed and dipped into clean ethanol for around 10 s. this was repeated twice before drying of the film. UV/Ozone treatment (1h) was used in order to oxidize the precursor as well as to remove polymer residues.

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Example 4

The antimicrobial activity of the glass slides containing silver nanoarrays as produced according to Example 1 was carried out by agar diffusion method and viable cell count method. The sensitivity of bacterial strains (Gram-positive and Gram-negative bacteria) commonly present in food products and native microflora from chicken to the glass slides containing silver nanoarrays were determined by the agar diffusion method. Prior to use glass

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slides containing and not containing silver nanoarray were sterilised in a laminar flow using UV. The slides were then aseptically placed on the surface of the inoculated Muller Hinton agar (MHA) with 0.1 ml of inocula containing indicator microorganisms in the range of 10^6 CFU/ml. The following bacterial strains were used: *Escherichia coli* (*E. coli*): (NCIMB 11943), *Staphylococcus aureus* (*S. aureus*): (NCIMB 13062), *Bacillus cereus* (*B. cereus*): (NCIMB 9373) and *Pseudomonas fluorescences* (*Ps. fluorescences*): (NCIMB 9046). A microflora isolated from raw chicken sourced locally was also used. Each strain was subcultured twice in 10 mL of Muller Hinton Broth and incubated at 30 for *Ps. Fluorescens* and *B. cereus* or 37°C for *E. coli* and *S. aureus*, respectively, for 18 h to reach a final concentration of 10^9 CFU/mL. After incubation, culture was then diluted in sterile maximum recovery diluent (Oxoid, UK) to obtain a final cell density of $\sim 10^6$ CFU/mL. The sensitivity to the silver nanoarray antimicrobial glass slides was defined by the area of the inhibition zone produced.

To test the antimicrobial activity of glass slides containing silver nanoarrays using a viable cell count method; glass slides (1.7 cm x 2.5 cm) containing silver nanoarrays were placed in individual sterile flasks to which 30 ml of inoculums, containing indicator microorganisms in the range of 10^6 CFU/ml, were added. Inoculums of cell suspension in a flask with glass slides without silver nanoarrays were used as a control. The flasks were incubated using an orbital shaker and rotated at 168 rpm at 30 or 37°C and aliquots of 1.5 ml were taken from the flasks and optical density at 610 nm measure every using a UV-visible spectrophotometer. The changes in the optical density were monitored for up to 36 hr.

The susceptibility of the native microflora obtained from chicken and pure bacterial strains to the silver nanoarray glass slides as determined by the agar diffusion method are presented in Table 1. The silver nanoarray showed antimicrobial effect against all bacteria tested (Gram (+) and Gram (-) bacteria) including chicken microflora. Inhibition zones were noticed in all bacterial strains tested and the most susceptible microorganism to the silver nanoarrays was *Ps. fluorescence* followed by *S. aureus*. A spore forming bacteria (*Bacillus cereus*) was also inactivated, indicating that the silver nanoarrays are a powerful antimicrobial with a wide spectrum. After measuring the inhibition zone area, plates were stored for up to 7 days and the inhibition zone area was measured again. The area of the inhibition zone did not change after 7 days storage indicating that the bacteria are inactive and possibly death and the effect of the silver nanoarrays is biocide and not only bacterisotatic.

The antimicrobial activity of the glass slides containing silver nanoarrays against *Ps. Fluorescens* and *S. Aureus* using a viable cell growth in liquid media is shown in Table 2. The

silver nanoarrays delayed significantly the outgrowth of the bacteria tested compared to control samples.

5 **Table 1:** Antimicrobial activity of silver nanoarrays against pure culture and chicken microflora

Bacterial strain	Inhibition zone area* (cm ²)
<i>Pseudomonas Fluorescens</i>	7.8
<i>E. coli</i>	5.0
<i>Staphylococcus aureus</i>	7.1
<i>Bacillus cereus</i>	5.7
Chicken microflora	6.6

Initial area of silver nanoarray slides = 4.20 cm². The results presented are the average of 2 measurements.

10 **Table 2:** Antimicrobial activity of glass slides containing silver nanoarrays against Gram (+) and Gram (-) bacteria.

Bacterial strain	OD at 610 nm							
	Time (hr)							
	0		8		24		36	
	C	SN	C	SN	C	SN	C	SN
<i>Ps. fluorescens</i>	0.004	0.004	1.024	0.004	1.631	0.0073	ND	0.011
<i>S. aureus</i>	0.004	0.004	1.12	0.009	1.745	0.012	ND	0.015

15 C: glass slides without silver nanoarrays
 SN: glass slides containing silver nanoarrays
 ND: not determined

Example 5

A beef steak was packaged in a Styrofoam tray, and the steak and tray were wrapped within the activated film formed according to Example 3. The surface bearing the nanoarray of nanostructures covers an area of approximately 5cm^2 , with the nanostructures provided by nanodots having an average diameter of approximately 20nm, and arranged at a density of approximately 1×10^8 nanodots/ cm^2 . As packaged, the surface bearing the nanoarray of silver chloride nanodots abuts a top surface of the steak. A similar steak was packaged in similar packaging but without the array of nanodots on the film. Both packages were stored for five days at refrigeration conditions, and the microbial load on the steaks sampled at days 3, 4, and 5.

Example 6

A beef steak was packaged in a Styrofoam tray, and the steak and tray were wrapped within the activated film formed according to Example 3. Prior to packaging within the film, a stiff polymeric insert was placed on a top surface of the meat, the insert bearing a nanoarray of silver chloride nanostructures on a surface of the insert that bears against the meat. The surface bearing the nanoarray of nanostructures covers an area of approximately 5cm^2 , with the nanostructures provided by nanodots having an average diameter of approximately 20nm, and arranged at a density of approximately 1×10^8 nanodots/ cm^2 . A similar steak was packaged in similar packaging but without the array of nanodots on the film insert. Both packages were stored for five days at refrigeration conditions, and the microbial load on the steaks sampled at days 3, 4, and 5.

Example 7

A salmon steak was packaged in heat sealable poly-coated foil paper packaging material bearing a nanoarray of silver chloride nanostructures on an interior surface of the material. The surface bearing the nanoarray of nanostructures covers an area of approximately 5cm^2 , with the nanostructures provided by nanodots having an average diameter of approximately 20nm, and arranged at a density of approximately 1×10^8 nanodots/ cm^2 . As packaged, the surface bearing the nanoarray of silver chloride nanodots abuts a top surface of the salmon steak. A similar steak was packaged in similar packaging but without the array of nanodots on the film insert. Both packages were stored for five days at refrigeration conditions, and the microbial load on the steaks sampled at days 3, 4, and 5.

The invention is not limited to the embodiments hereinbefore described which may be varied in construction, detail and process step without departing from the spirit of the invention.

Claims

1. A package comprising packaging material defining an enclosed space suitable for containing an item susceptible to microbial growth or spoilage, an interior of the package comprising at least one antimicrobial surface bearing an ordered nanoarray of metal or metal oxide nanostructures.
2. A package as claimed in Claim 1 in which the ordered nanoarray of metal or metal oxide nanostructures is formed by self-assembly from a microphase separated block copolymer in which one of the polymers selectively incorporates a metal ion salt prior to treatment of the block copolymer to oxidise the metal ion salt and remove the polymers
3. A package as claimed in any preceding Claim in which the surface bearing a nanoarray of metal or metal oxide nanostructures is part of an interior surface of the packaging material.
4. A package as claimed in any of Claims 1 to 3 in which the nanoarray of nanostructures has a density on the surface of at least 1×10^8 nanostructures/cm².
5. A package as claimed in any of Claims 1 to 4 in which the nanostructures have an average diameter of from 10-50nm.
6. A package as claimed in any preceding Claim in which the antimicrobial surface is formed of a polymeric material.
7. A package as claimed in any preceding Claim and selected from a tray, a carton, a bag, a pouch, a bottle, and a wrapper.
8. A package as claimed in any preceding Claim, in which the antimicrobial surface bearing the ordered nanoarray of metal or metal oxide nanostructures has a surface area of at least 5cm².
9. A package as claimed in any preceding Claim containing an item susceptible to microbial growth or spoilage.
10. A package as claimed in Claim 9 in which the item susceptible to microbial growth or spoilage is a comestible product.

11. A package as claimed in any preceding Claim in which at least a portion of the at least one antimicrobial surface is in contact with at least a portion of the item.
12. A package as claimed in any preceding Claim, in which the metal is selected from a transition metal or a lanthanide.
13. A packaging material in the form of a sheet or film having a first face and a second face, in which at least a portion of one of the first or second faces of the film comprises a surface bearing an ordered nanoarray of metal or metal oxide nanostructures.
14. A packaging material as claimed in Claim 13 in which the ordered nanoarray of metal or metal oxide nanostructures is formed by self-assembly from a microphase separated block copolymer in which one of the polymers selectively incorporates a metal ion salt prior to treatment of the block copolymer to oxidise the metal ion salt and remove the polymers
15. A packaging material as claimed in Claim 13 or 14 in which the surface bearing a nanoarray of metal or metal oxide nanostructures is part of an interior surface of the packaging material.
16. A packaging material as claimed in any of Claims 13 to 15 in which the nanoarray of nanostructures has a density on the surface of at least 1×10^8 nanostructures/cm².
17. A packaging material as claimed in any of Claims 13 to 16 in which the nanostructures have an average diameter of from 10-50nm.
18. A packaging material as claimed in any of Claims 13 to 17 in which the antimicrobial surface is formed of a polymeric material.
19. A packaging material as claimed in any of Claims 13 to 18 and selected from a tray, a carton, a bag, a pouch, a bottle, and a wrapper.
20. A packaging material as claimed in of Claims 13 to 19, in which the antimicrobial surface bearing the ordered nanoarray of metal or metal oxide nanostructures has a surface area of at least 5cm².
21. A packaging material as claimed in any of Claims 13 to 20, in which the metal is selected from a transition metal or a lanthanide.

22. Use of a packaging material as claimed in Claims 13 to 21, as an antimicrobial agent.
23. A method of preventing or inhibiting microbial growth on a comestible item
5 contained within a package, which method employs a packaging material at least part
of which comprises a surface bearing a nanoarray of metal or metal oxide
nanostructures, the method comprising a step of partially or completely enclosing the
comestible item within the packaging material to form a package such that the surface
bearing the nanoarray of metal or metal oxide nanostructures is disposed on an
10 interior of the package.
24. A method of extending the shelf life of a packaged comestible item, typically a food
product, which method employs a packaging material at least part of which comprises
a surface bearing an ordered nanoarray of metal or metal oxide nanostructures, the
15 method comprising a step of enclosing the comestible item within the packaging
material to form a package such that the surface bearing the nanoarray of metal or
metal oxide nanostructures is disposed on an interior of the package.
25. A method of preserving a packaged comestible item, typically a packaged food
20 product, which method employs a packaging material at least part of which comprises
a surface bearing a nanoarray of metal or metal oxide nanostructures, the method
comprising a step of enclosing the comestible item within the packaging material to
form a package such that the surface bearing the nanoarray of metal or metal oxide
nanostructures is disposed on an interior of the package. The surface bearing the
25 nanoarray of metal or metal oxide nanostructures may be integrally formed with the
packaging material, or may take the form of an insert.
26. Use of a substrate having a surface bearing an array of metal or metal oxide
nanostructures as a packaging material for an item susceptible to microbial growth or
30 spoilage, especially a comestible item such as a food product.
27. Use of Claim 26 in which the substrate is a material suitable for packaging, such as a
polymeric, paper, or foil material, or a composite thereof.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/063710

A. CLASSIFICATION OF SUBJECT MATTER
INV. B65D81/28
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)
B65D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/53413 A1 (ICET INC [US]; SARANGAPANI SHANTHA [US]) 14 September 2000 (2000-09-14) pages 1-6; example 5	1-11, 13-20, 22-27
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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
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- "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 24 October 2013	Date of mailing of the international search report 06/11/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Jervelund, Niels
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/063710

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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