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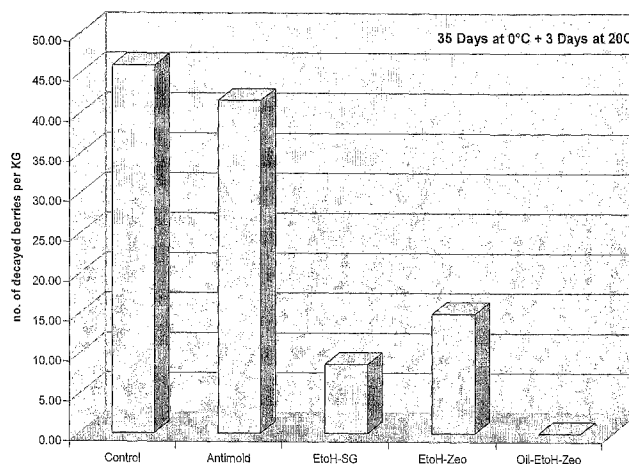


Figure 5

Control: Commercial Modified Atmosphere Packaging bags  
Antimold®: Ethanol based commercial treatment - product of Freund Corporation of Japan  
EtoH-SG: Ethanol-Silica gel compound - no essential oil  
EtoH-Zeo: Ethanol-zeolite compound - no essential oil  
Oil-EtoH-Zeo: Essential oil-ethanol-zeolite composition according to the invention

(57) Abstract: Active materials employing a composition containing essential oils adsorbed in combination with a solvent within a micro-porous solid material have been developed. The subsequent controlled release of essential oil vapour provides numerous applications including anti-microbial properties and extension of shelf life to packaged perishable goods. The active material may be presented in the form of a polymeric or natural fibre substrate coated or printed with the composition or in the form of granules or tablets optionally contained within a porous sachet.

## Active Materials incorporating Micro-porous solids and Essential Oils

This invention relates to active materials, in particular, but not exclusively, for packaging perishable goods, particularly perishable foodstuffs. The term “active materials” in this application is defined as materials which release essential oil vapour in a controlled manner over time. One application of such active materials is in offering protection of perishable goods from quality loss during storage and display throughout the supply chain.

In this application, “perishable goods” is defined as any good that requires special treatment and handling conditions to prevent or inhibit quality loss through microbiological, physiological or chemical spoilage. The term “fresh produce” is defined as harvested fruit, vegetables and cut flowers, uncooked meat and fish. Fresh produce is comprised within “perishable goods”. Processed foods, including, but not limited to, processed fresh fruit and vegetables, juices, drinks, dairy produce, cheese, cooked or smoked meat and fish, and potted ornamental plants, are similarly comprised within “perishable goods”.

The term “active packaging” is defined as packaging which has been specifically designed to change the atmosphere within packs of perishable goods in order to extend their shelf life, improve their safety or enhance their sensory properties.

Many fruits, vegetables and flowers are sensitive to ethylene which acts as a plant hormone that has various physiological effects on fresh produce. It accelerates respiration, leading to enhanced maturity and senescence, and to softening and ripening of a wide variety of agricultural commodities. To prolong shelf life and maintain acceptable visual and organoleptic quality, accumulation of ethylene in packs of perishable foodstuffs should therefore be mitigated either by placing an ethylene removal agent inside the pack or by incorporating an ethylene removal agent as a component of the active packaging.

An effective ethylene absorber consists of a solid support impregnated with potassium permanganate solution ( $\text{KMnO}_4$ ). However, due to the chemical properties of potassium permanganate, precautions must be taken to prevent contamination of the contents of the pack by contact with the chemical. Disposal of the packaging waste is a further disadvantage of the use

of such a product as an ethylene absorber. Use of other materials with ethylene absorbing capability and with fewer disadvantages would therefore be desirable.

Another factor contributing to food spoilage derives from microbial contamination on the food surface. This may arise from the foodstuff itself or from human contact with the foodstuff during harvesting or subsequent handling and processing. Packaging offering anti-microbial properties provides an effective solution for microbial contamination of the food surface from whatever source the contamination may have arisen. One of the most promising applications of active packaging is anti-microbial packaging film from which an active ingredient is released into the atmosphere surrounding the perishable goods or on to their surface thereby inhibiting growth of micro-organisms.

The effectiveness of currently developed active packaging materials is limited as active materials have hitherto generally been incorporated within the mass of the packaging film and this in turn has interfered with extrusion, often limiting active material content, and has impeded subsequent release of active material, thereby reducing efficacy.

The present invention has been made from a consideration of the foregoing problems and the disadvantages of known packaging materials and seeks to provide a solution to the undesirable effects of ethylene accumulation and microbial contamination on packaged perishable goods, in particular foodstuffs. The efficacy of different active packaging materials in extending freshness and improving quality of fresh fruits, vegetables and cut flowers have been evaluated.

According to one aspect of the present invention, we provide an anti-microbial composition comprising a micro-porous solid and an essential oil in which the essential oil is combined with a solvent in order to increase adsorption of essential oil within the pores of the micro-porous solid.

The solvent may be an alcohol, for example ethanol, or an alkane, for example pentane, hexane, heptane, octane, iso-octane or mixtures thereof.

It is a feature of this invention that the solvent, preferably ethanol, when used in this way to increase adsorption of essential oil, also enhances the anti-microbial efficacy of the composition.

The present invention addresses the limitations described above by combining micro-porous solids with essential oils in a bespoke process and then appropriately formulating the composition in such a way that it may be presented in different forms. Although by no means limiting, the presentations can include:

- Coatings, for example, on substrates such as packaging films
- Coatings, for example, on the face material of self-adhesive labels
- Granules which may, for example, be packed in porous sachets
- Tablets which may or may not be packed in porous sachets
- Substrates incorporating the composition within their mass

In all such presentations, the composition will emit essential oil vapour at a controlled rate over an extended period of time which expression when used herein is defined as a longer period than has hitherto been described using natural materials. This characteristic of the composition may find uses in many different fields in addition to anti-microbial applications. The rate of release of essential oil vapour from the composition may be varied by use of an appropriate micro-porous solid and of an appropriate process by which the essential oil is included within the pores of the micro-porous solid. In certain applications of this invention, a combination of benefits can be obtained. For example, the composition can be formulated within active materials which provide both anti-microbial protection of the packaged goods and absorb unwelcome odours released by the packaged goods. A further example of a combination of benefits is where the solvent used to increase adsorption of the essential oil on the micro-porous solid is selected for its own anti-microbial properties, being released as a vapour along with the vapour of the essential oil, thereby enhancing the anti-microbial efficacy of the active material.

In at least one embodiment, the micro-porous solid is a zeolite. The micro-porous solid may be selected from the group consisting of large-pore zeolites with channel free diameter from 12Å to 5.9Å or from the group consisting of medium-pore zeolites with channel free diameter from 5.9Å to 5.0Å. It will be noted that zeolites and essential oils are naturally occurring, non-toxic materials and friendly to humans and to the environment. The use of a combination of zeolites

and essential oils according to this embodiment has been found to extend storage life of vegetables, fruits, flowers and other perishable produce.

5 In another embodiment, the micro-porous solid is a form of clay, preferably selected from the group consisting of montmorillonite KSF clay or montmorillonite K10 clay, and mixtures thereof.

10 In a third embodiment, the micro-porous solid is a form of diatomite, preferably selected from the group consisting of diatomaceous earths which consist principally of amorphous silica. Diatomaceous earth deposits are usually categorised based upon their fresh water or salt water origin. After mining and drying at temperatures up to 650°C, both the chemical composition and the physical structure of diatomaceous earths make them of great commercial value for a wide spectrum of uses, including filter aids, functional fillers, carriers for active ingredients and diluents, and aggregates. In a few regions of the world, the diatomaceous earth deposits have  
15 been formed in sufficient thickness and purity to be mined for many uses beneficial to mankind, including practising this invention.

In yet a fourth embodiment, the micro-porous solid is a form of cellulose fibre produced from natural materials including, but not limited to, the bark of trees, which may be selected, for  
20 example in the form of a micro-porous chip, granule, powder, or mat on to which the essential oil combined with a solvent may be adsorbed and then, where necessary, the resulting composition may be converted into granules, tablets, coatings or printing inks.

Advantageously, the micro-porous solid is an ion-exchanged form of zeolite or clay, as the  
25 properties of the clay or the zeolite are affected by the nature of the exchangeable cation, for example, without being limited by the following examples, pore size (in the case of zeolite), interlaying spacing (in the case of clay), water absorption capacity, catalytic properties, adsorption affinity to organic compounds, tactoid size i.e. number of layers in the flock, anti-microbial activity (e.g. Cu-clay), and acidity of the surface. For example, the micro-porous solid  
30 may be a cation-exchanged zeolite or clay with metals, such as  $K^+$ ,  $Na^+$ ,  $Li^+$ ,  $Cs^+$ ,  $Be^{+2}$ ,  $Cr^{+3}$ ,  $Ce^{+3}$ ,  $Cu^{+2}$ ,  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Ag^+$ ,  $Ba^{+2}$  or  $Zn^{+2}$ , and mixtures thereof.

In one preferred embodiment, the micro-porous solid is selected from the group consisting of hydrophobic organophilic pentasil zeolites with Si:Al ratio higher than 10.

5 In another preferred embodiment, the micro-porous solid is selected from the group of meso-porous solids such as silica gel  $\text{SiO}_2$  and aluminum oxide  $\text{Al}_2\text{O}_3$ .

Different presentations of the composition comprising the invention may use different particle sizes of micro-porous solid. The particle size of the micro-porous solid is generally less than 1000 microns ( $\mu$ ) although larger particle sizes may be used in certain applications. For example, 10 presentation as a coating or within the mass of a substrate is preferably practised with particle sizes less than 25 microns whereas presentation as a tablet is preferably practised with particle sizes between 100 microns and 500 microns, and as a granule with particle sizes between 200 microns and 1000 microns, although these ranges of particle size are by no means limiting.

15 In this invention, the term "essential oil" is defined as any concentrated, hydrophobic liquid containing volatile aroma compounds either obtained directly from aromatic herbs or aromatic plants ("natural oils"), or synthesized ("nature-identical oils") to be identical to those of natural origin. This invention has been practised with both natural oils and nature-identical oils with 20 equally effective results. An oil is "essential" in the sense that it carries a distinctive scent, or essence, of the plant.

The essential oil may be selected from the group consisting of thymol, carvacrol, eucaliptol, cinnamaldehyde, eugenol, menthol, cuminal, anethole, estragole, citronnellal, carvone, menthone, limonene, isoeugenol, bisabolol, camphor, geraniol, citral, and mixtures thereof, 25 although this list is by no means limiting.

Active packaging materials using this invention have been developed for ethylene removal and for releasing anti-microbial essential oils allowing the original qualities of fruits, vegetables, flowers and processed food to be maintained during an extended period. Amongst other 30 applications, this is often of crucial importance in developing the export of fresh products to distant markets.

For active packaging applications, the essential oil is typically oregano oil, thyme oil, lavandin oil, clove oil or cinnamon oil, although many other essential oils can be used. A source of these essential oils is Frutarom Industries Limited, a multi-national corporation traded on the Tel-Aviv and London stock exchanges, who offer a large variety of essential oils suitable for use in applications described herein. Although it is possible to use synthetic essential oils such as thymol or carvacrol, natural essential oils are preferred, firstly because they are natural and hence environmentally attractive in fresh produce packaging, and secondly because they are often liquid at ambient temperatures whereas the synthetic equivalent may often be solid at ambient temperatures.

The composition may further comprise one or more additional ingredients selected from the group consisting of protective colloids, adhesives, binding agents, chelating agents, thickening agents, thixotropic agents, suspension aids, surfactants, penetrating agents, stabilizing agents, sequestering agents, anti-foam agents, antioxidants, natural or synthetic seasonings and/or flavours, dyes and/or colorants, vitamins, minerals, nutrients, enzymes, insecticides, deodorants, and mixtures thereof.

The composition may comprise a granular product in the form of a powder, pellets, beads, or granules that may be presented in a porous sachet.

The granular product may then be compressed into a tablet. Smaller tablets may be presented in a porous sachet whereas larger tablets may be used without any packaging within circulating air systems where anti-microbial activity is advantageous, e.g. storage depots for fresh produce, air conditioning systems, including those used within aircraft, hotels, and hospitals. The granules are dried until they are substantially free of any surface liquid, then mixed with a powdered binding agent such as polyethylene glycols, preferably of molecular weight between 3000 and 6000, and then compressed causing the granules to adhere to each other for the lifetime of the tablet.

We have found that the composition according to the first aspect of the invention has many uses in applications where anti-microbial activity is beneficially released from the composition over an extended period of time.

For example, the composition may be used:

- 5       • for protecting food products from bacterial and fungal infection during storage by dusting with the composition prepared as a powder presentation. The food products may be fresh fruits and vegetables, fresh cut fruits, vegetables or flowers, semi-processed food or fully processed food.
- for providing anti-microbial protection of agricultural crops by such means as soil microbial sterilisation or over-spraying of the crops with the composition.
- 10     • for providing anti-microbial protection in medical hand lotions and cleaning or sanitizing agents for medical use
- for providing anti-microbial protection in air filtration systems or scrubbers in which it is required to impart anti-microbial activity to the filtered air without damage to the health of those subsequently inhaling the filtered air or without damage to the environment.
- 15     • for masking of bad odours over an extended period which is beneficial to those working in or living close to the source of the bad odours such as livestock farms, abattoirs, and disposal sites for animal and human waste. The composition in powder form may also be incorporated into animal feedstuffs to prevent microbial development within the gastro-intestinal tract.
- 20     • for repelling unwanted pests such as, but not limited to, slugs, snails and insects from agricultural crops, horticultural nursery stock, sports turf and garden plants.

According to a second aspect of the present invention, we provide a packaging material impregnated with or coated or printed with the anti-microbial composition according to the first aspect of the invention. In preparing such a coating or printing ink, we have found that the inclusion of a suspension agent such as those provided within the Solsperse® range manufactured by Lubrizol Corporation has been beneficial in suspending the micro-porous solid. In the embodiment where the packaging material is coated or printed with an anti-microbial composition, it can subsequently be converted into different packaging products including filmic bags, pouches and sachets including reclosable “zipped” versions or used as a face material in labelstock constructions suitable for subsequent conversion into self-adhesive labels. In this latter application, the anti-microbial coating or printing ink is located on the opposite side of the

face material to the pressure sensitive adhesive. Typically, the self-adhesive label will be applied to the internal wall of the bag, pouch or sachet containing the perishable goods.

It will be obvious, but will be stated nevertheless, that in the case where the active packaging has been produced by coating or printing the composition on a packaging film, then following conversion of the active packaging material into a suitable packaging format such as, for example, filmic bags, pouches and sachets by whatever process and of whatever configuration, the coated or printed side of the active packaging substrate is always located on the inner surface of the pack containing the perishable foodstuff. Furthermore, it is not necessary for the active packaging material to be flood coated with the composition. The composition may be strip coated, pattern coated or printed in order to provide the economic and technical benefits of this invention. The strip or pattern coating or printing can be applied in such a way that the composition does not interfere with heat sealing of the active packaging substrate. In the case where the coating or printing is suitably pigmented or coloured, and the bag, sachet or pouch is made from a transparent filmic substrate, the coating or printing can be reverse printed or otherwise used to carry a marketing message providing, amongst other uses, information to the consumer.

We have found that packaging material impregnated with, coated with, or printed with the anti-microbial composition offers improved properties when used as packaging for perishable foodstuffs including properties such as ethylene removal, water permeability and anti-microbial activity, all of which are beneficial to the freshness and quality of packed perishable products.

We have found that the composition according to the second aspect of the present invention can also be used in the medical or veterinary fields as a packaging film where anti-microbial protection is required.

Our research programme has included:

- (a) testing the anti-microbial activity of zeolite/essential oil combinations against a wide range of target micro-organisms, and
- (b) investigating the physico-mechanical properties of different presentations of zeolite/essential oil combinations, and
- (c) studying the rate of release of essential oils from zeolite/essential oil combinations, and

- (d) assessing the efficacy of different uses of zeolite/essential oil combinations in different applications, and
- (e) evaluating the efficacy of ethylene adsorbing and anti-microbial releasing formulations of zeolite/essential oil combinations to extend freshness and improve quality of fresh fruits, vegetables and cut flowers, under laboratory and commercial conditions.

According to another aspect of the present invention, the micro-porous solid, the essential oil and solvent are combined together in a bespoke process resulting in a slurry. The slurry may be dried by various means including movement of air at ambient or higher temperatures, fluid bed drying, spray drying, freeze drying, vacuum filtration, regular filtration, centrifuging, pan granulation, and extrusion granulation, in order to produce active packaging granules or beads. Preferably, the granules or beads are of diameter between 1mm and 5mm, more preferably around 3mm. It has been found that these active packaging granules or beads when packed in a porous sachet and placed within packs of fruits, vegetables or other perishable foodstuffs, offer similar anti-microbial protection to that obtained by coating or printing the composition on a packaging substrate.

In this embodiment, the porous sachet is preferably made from materials based upon natural fibres such as paper, or upon polymeric materials manufactured from petroleum, renewable, or sustainable sources, or upon combinations of natural fibres and polymeric materials. By way of example only, appropriate materials are heat sealable beverage filter paper as used to make tea bags, interwoven polymeric fibre materials such as those made from viscose, polyester, polypropylene, polyethylene (e.g. Tyvek®), which are sufficiently porous to permit the passage of essential oil vapour emanating from the granules located within the sachet into the pack of perishable goods to provide an anti-microbial effect, and to permit the passage of ethylene and undesirable odours into the sachet to be adsorbed on the active packing granules or beads without allowing any part of the active packing granules or beads to escape through the pores of the sachet into the pack of perishable goods. It will be noted that the material from which the porous sachet is made should comply with food contact legislation, e.g. FDA 21 CFR 176.170 within the USA, or within the UK, implementation of European Commission Directives is enacted by Statutory Instrument No. 1376 "The Plastic Material and Articles in Contact with Food Regulations 1998" and its subsequent amendments.

By way of example only, it has been found that approximately 3 grams of zeolite after conversion into active packaging granules or beads and placed within a porous sachet according to this invention offers extended protection to packs containing 7 kilograms of grapes. This can be seen from the experimental results shown in Figure 5. However, if the combination of zeolite and essential oil, after appropriate formulation, is coated or printed upon a packaging film according to this invention, the quantity of zeolite required for similar extended anti-microbial protection may be reduced due to the greater surface area of zeolite exposed to the grapes. After drying, the quantity of essential oil adsorbed into the micro-pores of the zeolite may be up to 35% by weight, preferably 10 to 35% by weight, more preferably 10 to 30% by weight, still more preferably 10 to 25% by weight, even more preferably 15-25% by weight. This can be seen from the experimental results shown in Figures 6, 7 and 8.

Higher quantities of essential oil will be adsorbed into a micro-porous solid selected from the group consisting of large-pore zeolites with channel free diameter from 5.9Å to 12Å, such as Clinoptilolite, Beta, Linde X, Linde Y, Linde L, or Mordenite, and mixtures thereof, preferably NaX, NaY. Lower quantities of essential oil will be adsorbed into a micro-porous solid selected from the group consisting of medium-pore zeolites with channel free diameter from 5.0Å to 5.9Å, such as ZSM-5, Silicalite, Ferrierite types, Linde-T, Merlinoite types, or Linde W, and mixtures thereof.

It has been found that the addition of a suitable solvent, for example an alcohol such as ethanol or an alkane such as pentane, hexane, heptane, octane, iso-octane or a mixture thereof, mixed with the essential oil assists in the adsorption of the essential oil into the pores of the zeolite, whether subsequently presented as a coating or as a granule or tablet. The adsorption of an essential oil, in this example, thyme oil, when assisted by the addition of different solvents, ethanol and hexane, is compared in Figures 9 and 10.

The present invention has been found to offer controlled release of essential oils from micro-porous solids during longer periods than has hitherto been described using natural materials. This has enabled the invention, in addition to the preservation of perishable goods, to find further application for use as a mollusc repellent and as an insect repellent.

Thus, from another aspect, the invention provides an insect or mollusc repellent impregnated or coated with the composition according to the invention. These applications are of particular interest in the ornamental nursery market and the home and garden markets in those countries where the use of molluscicides and insecticides is declining in favour of natural alternative remedies such as those described here. Different types of essential oil may be required for each field of application. Mollusc repellent activity has been confirmed using pine oil, cedarwood oil and garlic oil. Insect repellent activity has been confirmed using aniseed oil, lemon eucalyptus oil, cedarwood oil, geranium oil and lemongrass oil.

Zeolites are naturally occurring or synthetically produced hydrated aluminium silicates which form a regular crystal lattice and release water at high temperature.

- Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many commercial applications where uniformity and purity are essential. However, we have found naturally occurring zeolites to be entirely suitable for the practice of this invention.
- Synthetic zeolites can be manufactured in a uniform, phase-pure state and in structures offering desirable properties which do not appear in nature. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts.

Typically, naturally occurring zeolites present lower Si:Al ratios than synthetic ones.

Zeolites are polar in nature and certain cations (sodium, potassium, lithium or calcium or any combination thereof) are implanted by ion exchange. The dehydrated crystals are interlaced with regular spaced channels of molecular dimension usually ranging from 2Å to 9Å. Non polar zeolites are synthesized by de-alumination of polar zeolites. This is done by treating the zeolite with steam at elevated temperatures, greater than 500°C. This high temperature heat treatment breaks the aluminium-oxygen bonds and the aluminium atom is expelled from the zeolite framework.

In addition to being naturally occurring or synthetically manufactured, zeolites may differ in the following important respects:

- Type X vs Type Y.

X and Y zeolites have the same structure but X zeolites have a lower Si:Al ratio (1.0-1.5) than Y zeolites (1.6-3.0)

- Hydrophilic vs hydrophobic
- Pore size and pore system dimensionality
- Particle size

10 We have found that this invention can be practised using zeolites of many different types and characteristics, i.e.

- naturally occurring
- synthetically manufactured – it is possible to manufacture desirable zeolite structures which do not occur in nature e.g. Zeolite A

15

- type X allowing comparatively higher quantity of active essential oil to be adsorbed
- type Y allowing comparatively lower quantity of active essential oil to be adsorbed
- hydrophilic for quicker release (typically up to 60 days) of active essential oil vapour
- hydrophobic for slower release (typically up to a year or more) of active essential oil vapour due to the oil being more strongly bound in the zeolite structure

20

- pore sizes of diameters varying from 3Å to 12Å
- particle sizes varying up to 1000µm where smaller particle sizes are preferred for coating and printing ink formulations and larger particle sizes may be used in granular and tablet preparations.

25 The efficacy of active packaging is based upon a number of different parameters including:

- porosity control (e.g. gas pressure release and gas composition balance);
- polymer permeability control (e.g. gas composition balance and temperature compensation);
- melting of waxes (e.g. temperature compensation);
- 30 • inorganic or organic oxidation (e.g. O<sub>2</sub> scavenging, O<sub>2</sub> permeation barrier, O<sub>2</sub> indicator, CO<sub>2</sub> generation and ethylene scavenging);

- enzyme catalysis (e.g. oxygen scavenging);
- acid and base reaction (e.g. CO<sub>2</sub> absorption, CO<sub>2</sub> generation and odour absorption);
- adsorption (e.g. taint removal, O<sub>2</sub> scavenging, ethylene scavenging and water removal);
- absorption (e.g. condensation control and drip collection); hydrolysis (e.g., SO<sub>2</sub> release);
- 5     • desorption (e.g. ethanol, hinokitiol and water release); and
- organic reactions (e.g. ethylene removal and O<sub>2</sub> barrier)

10     Polymeric and natural fibre substrates of many types with different physico-chemical properties have been used by the inventor for the production of active packaging materials according to this invention e.g., polyethylene, polypropylene, polyester, polyamide and other polymeric substrates of petroleum and of plant "bio-polymer" origins, and mixtures and laminations thereof with each other or with natural fibre materials such as paper.

15     The adsorbing properties of micro-porous materials with various anti-microbial active essential oils (such as thymol, carvacrol, eugenol and many others) have been investigated. Furthermore, the effect of water content, calcination temperature, particle size, solid content and physical form, on the activity of the composition as ethylene adsorber and as anti-microbial releasing agent, have been studied using different micro-porous materials, e.g. large-pore zeolites; medium-pore zeolites; small-pore zeolites; micro-porous clays; diatomaceous earths, ion-exchanged zeolites;

20     active micro-porous solids and hydrophobic pentasil zeolites.

Essential oil/zeolite adducts have been prepared by gas-solid reaction. The crystal structure, host:guest ratio, and the release rate of the active ingredient from the zeolite complex within the active packaging, have been determined by ourselves under various humidity conditions.

25     From yet another aspect of the invention, a process for preparing slurry compositions comprising essential oils, solvents, and micro-porous solids has been developed. To a solution of an essential oil in a solvent is added a micro-porous solid. The slurry composition is preferably stirred. A suspension agent may be added when the slurry composition is subsequently to be

30     incorporated in a coating or printing ink. The mixture may be cooled to room temperature. From this slurry composition, different presentations of the composition may be prepared.

If it is required to present the composition as a coating or a printing ink, the slurry composition may be added directly to a binding agent which has been dissolved in an organic solvent. The binding agent and solvent must be compatible with the components within the slurry. A suitable binding agent is DSM NeoResins product NeoCryl B-723 dissolved in ethyl acetate.

5

If it is required to obtain the composition presented as a dry material, for subsequent packing, for example, within a porous sachet, the slurry is vacuum filtered and the precipitated solid is washed by a small quantity of cold solvent and then dried at room temperature, for example vacuum dried.

10

These and other benefits and advantages of the invention in its various aspects will be more fully understood from the following descriptions given by way of example only with reference to the accompanying drawings in which:

15 **Figures 1 to 4** show the rate of loss of an essential oil (thymol) from different micro porous solids;

**Figure 5** shows the results of a comparative trial of five different products offering antimicrobial properties including the composition according to the invention;

20

**Figures 6 to 8** show the rate of loss of an essential oil (thymol) from different types of zeolite using different adsorbed amounts of essential oil-ethanol.

25 **Figures 9 and 10** show the rate of loss of an essential oil (thymol) from different types of zeolite using two different solvents to assist adsorption of the essential oil.

### Process

30 Dissolve 35kg of synthetic thymol in 30 litres of ethanol (typically denatured in such a way as to allow subsequent food contact use) and add the solution to 35kgs of hydrophilic type X zeolite as supplied by Grace Davison under their trade name SYLOSIV A10 (pore openings of approximately 10Å, particle size approximately 4µm). After evaporation of the ethanol, the

process will differ whether the composition of zeolite and essential oil is required as a granule or as a coating for packaging films.

In the case of the presentation of the active packaging as a granule or bead, 17 kg of calcium alginate or alternatively pectin are added to the slurry as coating agents, and finally 900 litres of water are added and mixed until homogeneity. The resulting mixture is then dried by any means which does not involve exposure to temperatures of greater than 40°C, and granulated.

In the case of the presentation of the active packaging as a film coating, the slurry is formulated with binding agents commonly used in the formulation of solvent-based inks and coatings such as that produced and marketed by DSM NeoResins as NeoCryl B-723

When crude natural thyme oil is used, due to its lower melting point compared to synthetic thymol, the quantity of ethanol required can be significantly reduced, thereby enhancing the attractiveness of the process.

### Example 1

In Figures 1 - 4, the rate of loss of an essential oil (in these figures, thymol) from different micro-porous solids is measured. The thymol is first adsorbed on a micro-porous solid in accordance with the bespoke process described in the current invention. The micro-porous solid containing the adsorbed thymol is then exposed to air under ambient conditions and the rate of loss of thymol is measured by extraction of the residual thymol from the micro-porous solid at regular time intervals and then subjecting the extract to gas chromatography – mass spectrometry (GC-MS) analysis. By this means, for different micro-porous solids, a relationship can be drawn over time of the quantity of residual thymol adsorbed within the micro-porous solid expressed as milligrams of thymol per gram of micro-porous solid. The line of best fit shown in each figure can then be determined by regression analysis.

It will be seen from Figures 1 - 4 that the rate of loss of thymol from different micro-porous solids varies according to the characteristics of the micro-porous solid that has been selected for each experiment. The line of best fit and the experimentally determined results at each time

interval can be clearly identified. In this way, the composition most appropriate to the requirements of a particular application in hand can be selected.

### Example 2

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In Figure 5, the results of a comparative trial are shown in which a commercial treatment (ANTIMOLD®, a product of Freund Corporation of Japan, in which ethanol is the active material) and a control are compared with three compositions as follows:

1. Ethanol adsorbed on to a silica gel (EtOH-SG)
- 10 2. Ethanol adsorbed on to a zeolite (EtOH-Zeo)
3. A combination of an essential oil and ethanol adsorbed on to a zeolite (Oil-EtOH-Zeo) according to the invention

In this trial, the three different compositions and the commercial ANTIMOLD® product were placed in bags containing table grapes and the bags stored for 35 days at 0°C and then 3 days at 20°C. together with a bag containing table grapes only as the control.. It will be evident from Figure 5 that the composition according to the invention comprising an essential oil adsorbed on a zeolite using an ethanol solvent has produced an outstanding result in which none of the grapes showed any microbial damage. This composition was produced by the bespoke process according to the invention.

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### Example 3

In Figures 6, 7 and 8, the weight of thymol that remains adsorbed on to the zeolite, expressed as % w/w of thymol to zeolite, is plotted against time for different types of zeolite. It will be seen that, by using this invention, it has been possible to prepare compositions containing unexpectedly high adsorbed levels of thymol on different types of zeolite and by selection of an appropriate zeolite, to control the rate of release of thymol from those compositions.

30 In Figure 6, the zeolite is a natural zeolite of particle size between 100 and 200 microns.

The relative proportions of the components are as follows:

1.0 gram of thymol in 2.0 mls of ethanol adsorbed on to 3.0 grams of zeolite

Air dried zeolite

Reference S

Oven dried zeolite at 105°C for 60 minutes

Reference SD

In Figure 7, the zeolite is a natural zeolite of particle size between 200 and 300 microns.

5 The relative proportions of the components are the same as in figure 6.

Air dried zeolite

Reference L

Oven dried zeolite at 105°C for 60 minutes

Reference LD

In Figure 8, the zeolite is the synthetic zeolite SylosivA10® of particle size between 3 and 5  
10 microns taken from hermetically sealed bags supplied by Grace Davison.

The relative proportions of the components are as follows:

1.0 gram thymol in 2 ml ethanol added to 3.0 grams of zeolite

Reference AL

1.5 grams thymol in 3 ml ethanol added to 3.0 grams of zeolite

Reference AH

2.0 grams thymol in 4 ml ethanol added to 3.0 grams of zeolite

Reference AHH

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#### Example 4

In Figures 9 and 10, the release rate of thymol from natural and synthetic zeolites was compared  
using ethanol and hexane (in separate experiments) as the solvent. The release rate was  
20 determined by measuring the remaining amount of thymol after different time intervals whilst the  
zeolite was exposed to the atmosphere in the laboratory.

In Figure 9, the zeolite is a natural zeolite of particle size between 100 and 200 microns.

The relative proportions of the components are as follows:

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1.0 gram thymol in 2 mls ethanol added to 3.0 grams of zeolite

Reference SE

1.0 gram thymol in 2 mls hexane added to 3.0 grams of zeolite

Reference SH

30 In Figure 10, the zeolite is the synthetic zeolite Sylosiv A10® of particle size between 3 and 5  
microns taken from hermetically sealed bags supplied by Grace Davison.

The relative proportions of the components are as follows:

1.5 grams thymol in 2 ml ethanol added to 3.0 grams of zeolite

Reference AE

1.5 grams thymol in 3 ml hexane added to 3.0 grams of zeolite

Reference AH

**CLAIMS**

1. An anti-microbial composition comprising a micro-porous solid and an essential oil in which the essential oil is combined with a solvent in order to increase adsorption of the essential oil within the pores of the micro-porous solid.
2. A composition according to claim 1 wherein the solvent enhances the anti-microbial properties of the composition.
3. A composition according to claim 1 in which the micro-porous solid is a zeolite.
4. A composition according to claim 1 wherein the quantity of essential oil adsorbed into the micro-porous solid is up to 35% by weight.
5. A composition according to claim 4 wherein the quantity of essential oil adsorbed into the micro-porous solid is from 10 to 35% by weight.
6. A composition according to claim 5 wherein the quantity of essential oil adsorbed into the micro-porous product is from 15-25% by weight.
7. A composition according to claim 1 wherein the micro-porous solid is selected from the group of meso-porous solids such as silica  $\text{SiO}_2$  and alumina  $\text{Al}_2\text{O}_3$ .
8. A composition according to claim 1 wherein the micro-porous solid is a form of diatomite.
9. A composition according to claim 1 wherein the micro-porous solid is a form of clay.
10. A composition according to claim 1 wherein the micro-porous solid is a form of cellulose fibre.
11. A composition according to any preceding claim wherein the essential oil is selected from the group consisting of thymol, carvacrol, eucaliptol, cinnamaldehyde, eugenol, menthol, cuminal, anethole, estragole, citronnellal, carvone, menthone, limonene, isoeugenol, bisabolol, camphor, geraniol, citral, and mixtures thereof.
12. A composition according to claims 1 to 11 wherein the solvent is selected from alcohols such as ethanol.
13. A composition according to claims 1 to 11 wherein the solvent is selected from alkanes such as pentane, hexane, heptane, octane, iso-octane or mixtures thereof.
14. A composition according to any preceding claim wherein the said composition further comprises one or more additional ingredients selected from the group consisting of protective colloids, adhesives, binding agents, chelating agents, thickening agents, thixotropic agents, suspension aids, surfactants, penetrating agents, stabilizing agents,

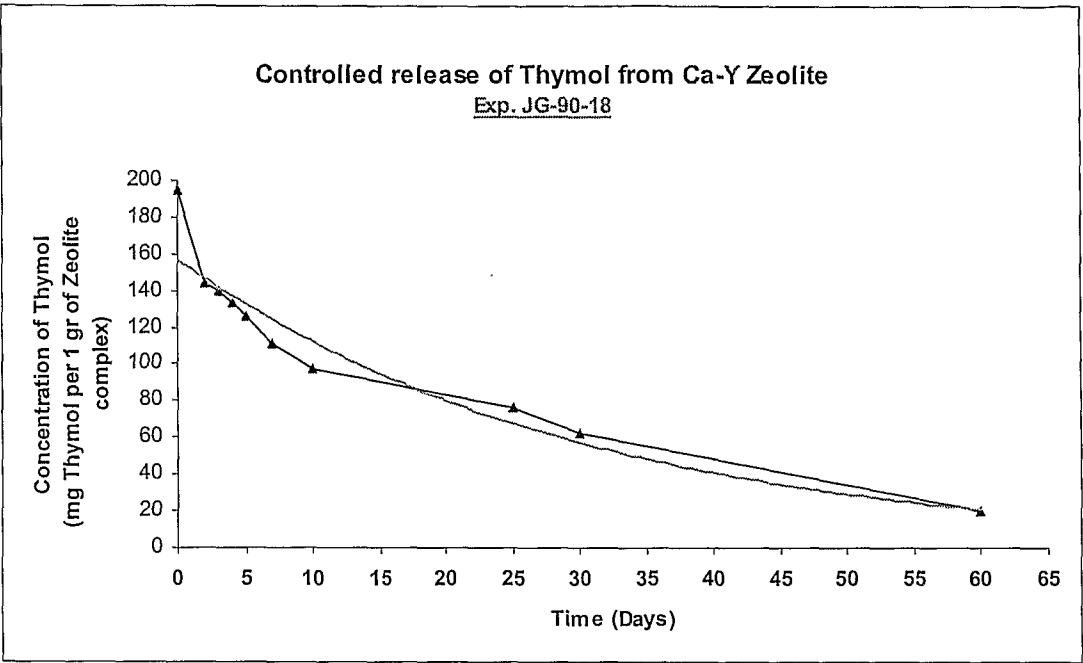
sequestering agents, anti-foam agents, antioxidants, natural or synthetic seasonings and/or flavours, dyes and/or colorants, vitamins, minerals, nutrients, enzymes, insecticides, deodorants, and mixtures thereof.

15. A composition according to any preceding claim comprising a granular product in the form of a powder, pellets, beads, granules, or tablets
16. A composition according to claim 15 packed in a porous sachet
17. A packaging material impregnated with the composition of any of claims 1 to 16
18. A packaging material coated or printed with the composition of any of claims 1 to 16
19. A self adhesive label converted from the packaging material of claim 17 or claim 18
20. An insect or mollusc repellent material impregnated with the composition of any of claims 1 to 16
21. An insect or mollusc repellent material coated with the composition of any of claims 1 to 16
22. A method for protecting food products from microbial infection by treatment with the composition according to any of claims 1 to 16.
23. A method according to claim 22 wherein the food products are fresh fruits and vegetables, fresh cut fruits and vegetables, semi-processed food or fully processed food.
24. A method for anti-microbial protection of agricultural crops by such means as soil microbial sterilisation or over-spraying of the crops using the composition according to any of claims 1 to 16.
25. A process for preparing an anti-microbial composition wherein adsorption of an essential oil within the pores of a micro-porous solid is increased by mixing the essential oil with a solvent.
26. A process according to claim 25 wherein the solvent is selected from alcohols such as ethanol.
27. A process according to claim 25 wherein the solvent is selected from alkanes such as pentane, hexane, heptane, octane, iso-octane or mixtures thereof.
28. A process according to any of claims 25 to 27 further including the step of converting the combination of micro-porous solid, essential oil and solvent into a material suitable for subsequent granulation by drying with air at ambient or higher temperatures.
29. A process according to claim 28 wherein the step of drying is selected from the group comprising fluid bed drying, spray drying, freeze drying, vacuum filtration, regular

filtration, centrifuging, and the step of converting to granules is selected from the group comprising pan granulation, and extrusion granulation.

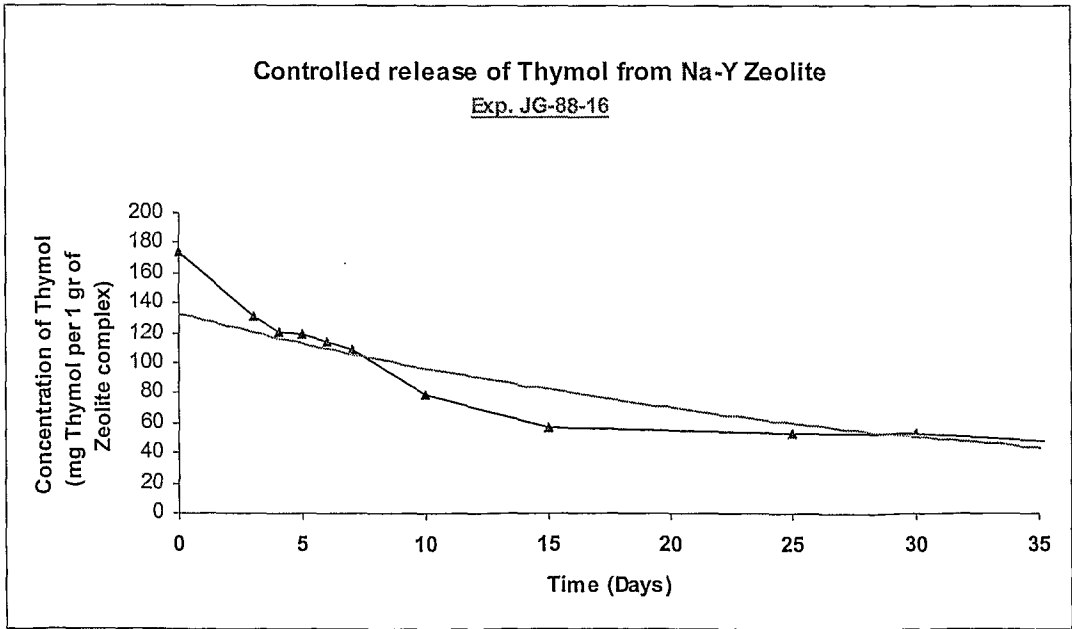
30. A packaging material made by the process according to any of claims 25 to 29.

Figure 1



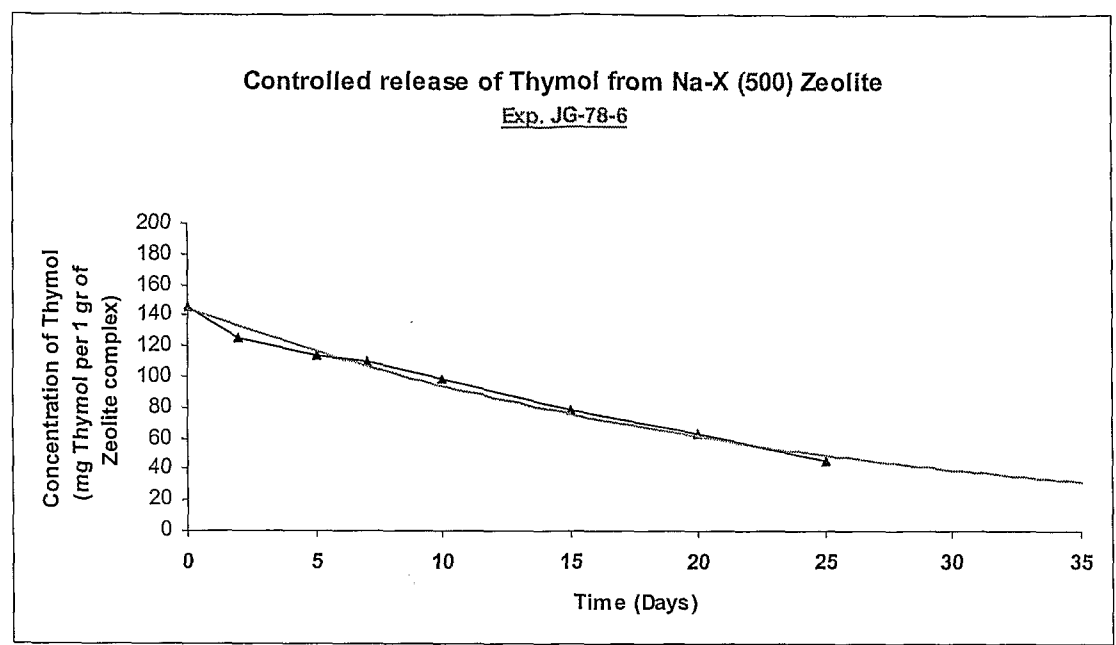
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Figure 2



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Figure 3



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Figure 4

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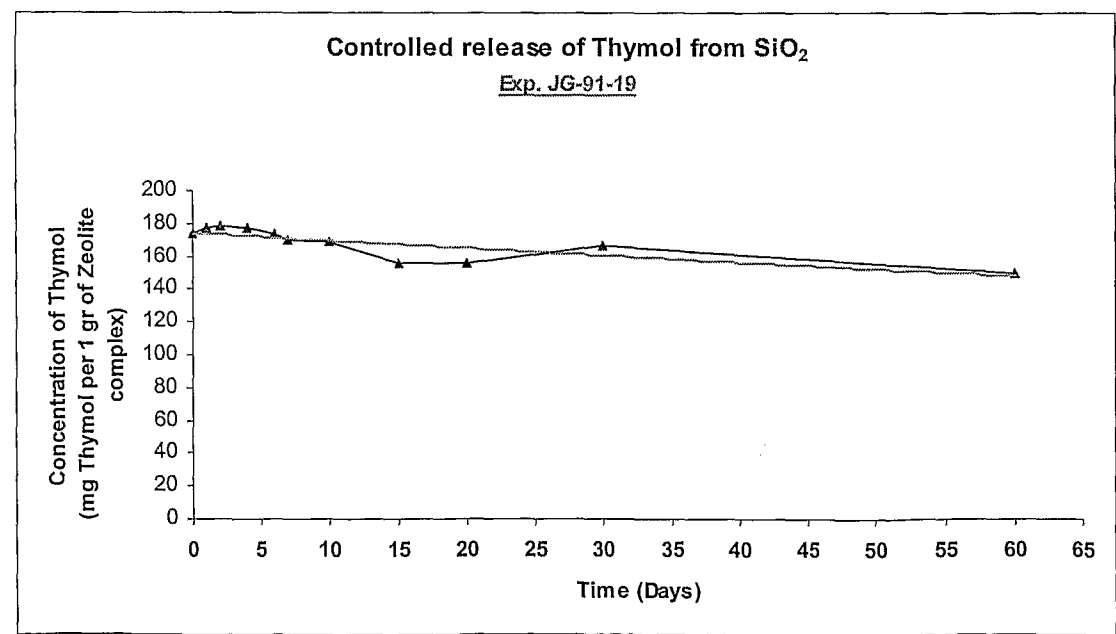
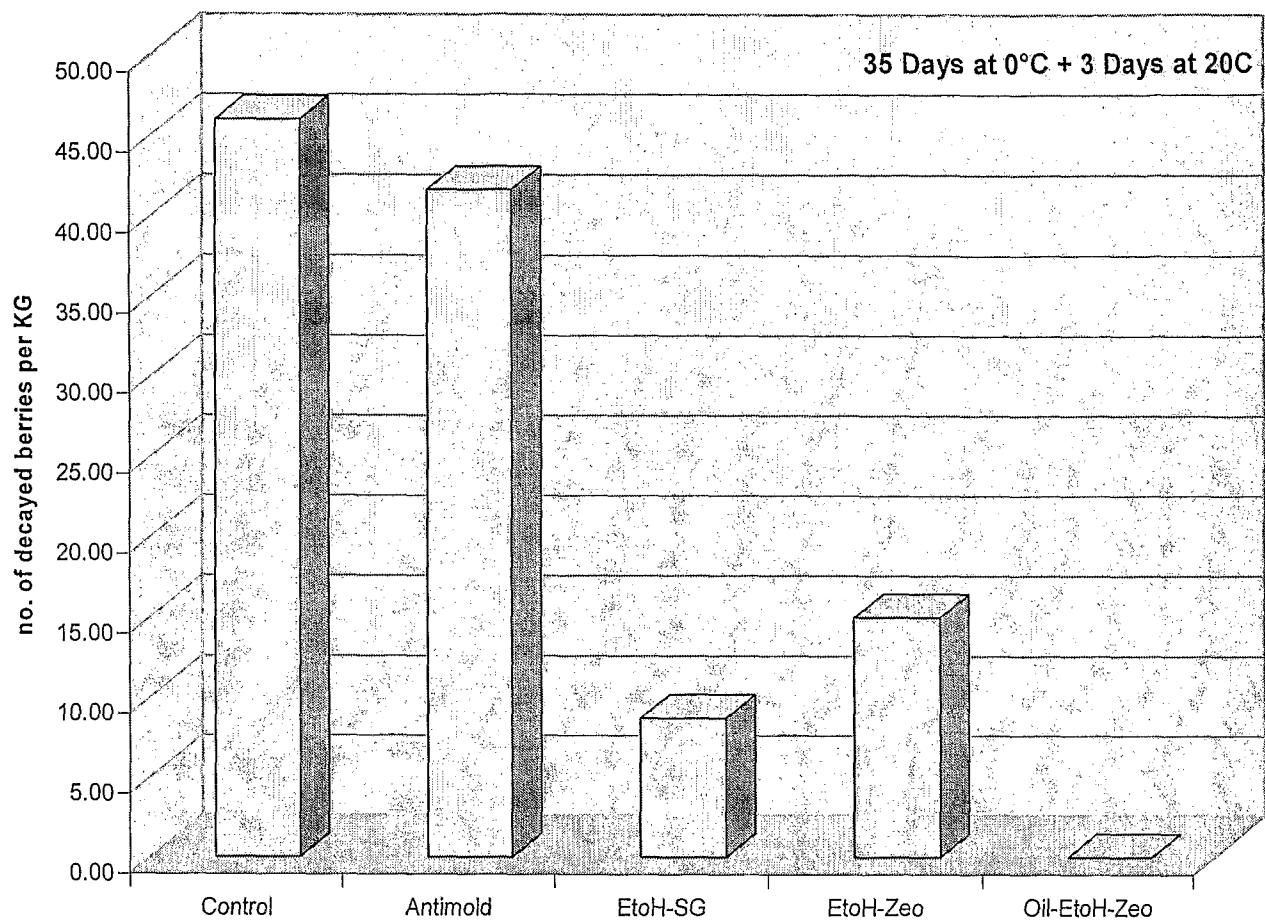


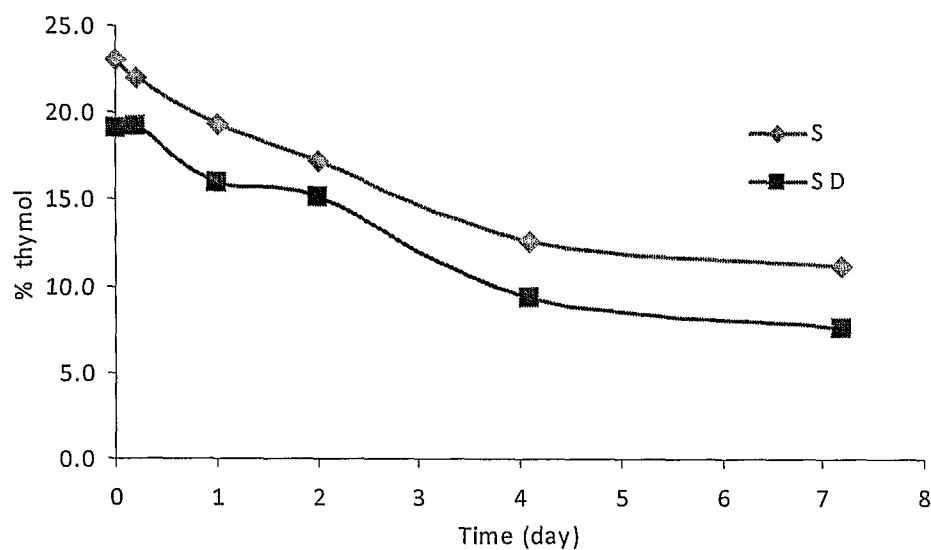
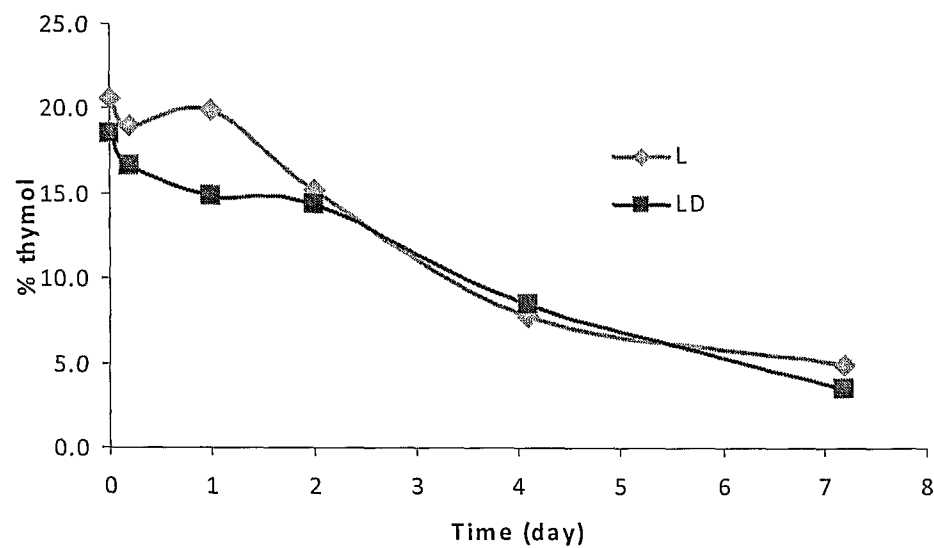
Figure 5



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Control: Commercial Modified Atmosphere Packaging bags  
Antimold®: Ethanol based commercial treatment – product of Freund Corporation of Japan  
EtoH-SG: Ethanol-Silica gel compound – no essential oil  
EtoH-Zeo: Ethanol-zeolite compound – no essential oil  
Oil-EtOH-Zeo: Essential oil-ethanol-zeolite composition according to the invention

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**Figure 6** Natural Zeolite 100-200 $\mu$ m**Figure 7** Natural Zeolite 200-300 $\mu$ m

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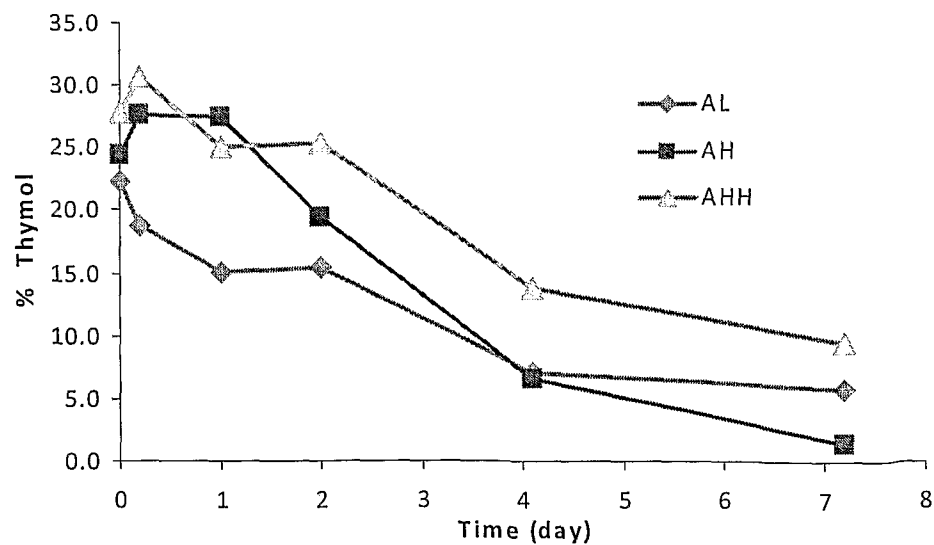
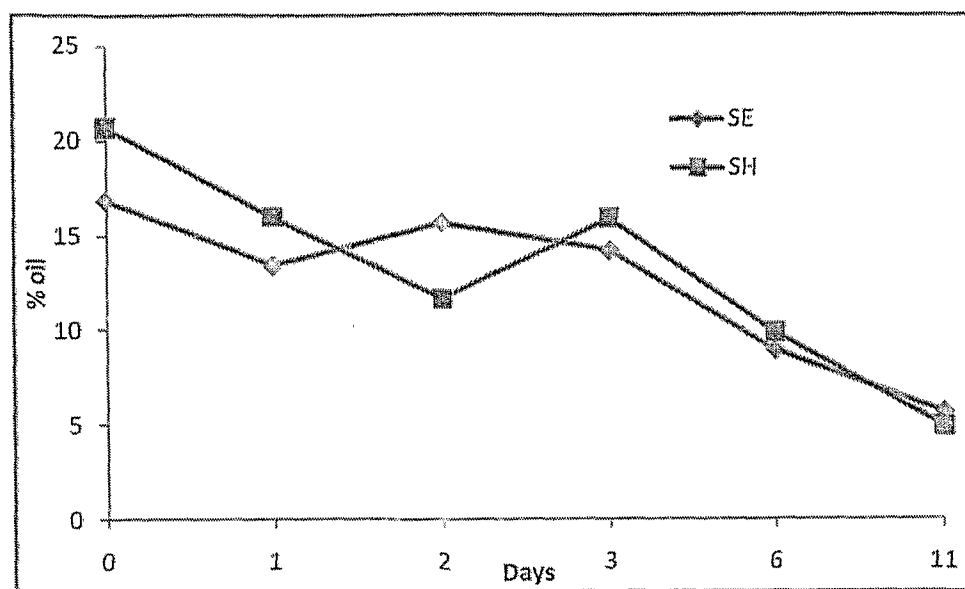
**Figure 8** Synthetic Zeolite 3-5 $\mu$ m

Figure 9 Natural Zeolite 100-200 $\mu$ m



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Figure 10 Synthetic Zeolite 3-5 $\mu$ m

