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(54) Title: GAS SENSOR

(57) **Abstract:** The invention relates to a gas sensor comprising at least one sensing material embedded in a substrate wherein the sensing material is a fluorescent material and the substrate is made out of a polymeric material that is suitable for film melt processing and has high gas permeability. The invention also relates to a process to prepare such a gas sensor, a packaging material comprising such a gas sensor and the use of such a packaging material. The invention also relates to a non-invasive method to determine the quality of a packaged product by the use of a gas sensor.



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GAS SENSOR

The invention relates to a gas sensor comprising a sensing material embedded in a substrate.

5 A gas sensor comprising a sensing material embedded in a substrate is for example known from WO01/63264. Herein a gas sensor is described wherein an oxygen sensitive dye is embedded in a substrate that consists of a fluoridated silicone polymer, more specifically a room-temperature vulcanizing, one part silicone rubber. A disadvantage of this type of substrates is that the material must be cured by atmospheric
10 moisture to obtain its final properties. This curing process is generally slow and additionally it limits the thickness of the substrate as when the substrate is too thick moisture can't reach the inside within a reasonable time; so either full through cure takes too long or the substrate is not fully cured. Another disadvantage of this type of material is that generally the mechanical integrity and the stability are unsatisfactory and that the costs are relatively
15 high.

 WO2004/077035 describes a gas sensor for detecting carbon dioxide combined with or without an oxygen sensor. The support material for the gas indicator is either based on sol-gel particles or is a sol-gel matrix. A disadvantage of this type of materials is that they are difficult to manufacture reproducibly and their production process
20 and the starting compounds are expensive.

 It is an object of the invention to overcome the above mentioned disadvantages and to make available a gas sensor that can be produced at relatively low cost, in a conventional production process and can be integrated into or combined with other materials at relatively high speed.

25 This object is reached by a gas sensor comprising at least one sensing material embedded in a substrate wherein the sensing material is a fluorescent material and the substrate is made out of a polymeric material that is suitable for film melt processing and has high gas permeability.

 Nowadays more and more objects are individually packaged. The reason
30 for packaging objects is varied. For example food and beverage products are packaged to protect them for example against damage and/or microbial spoilage during storage and transport. The pharmaceutical, medical and electronics industry require

sometimes individual packaging for different reasons. However whatever kind of object is packaged there was a reason to spend the additional costs for the packaging material and the packaging process. Thus it is also relevant to be able to determine whether the packaged object has still the desirable or sufficient quality what made the
5 packaging necessary.

A way to determine the quality of the packaged product without destroying the package has now been found and relates to a method that is able to determine the inside atmosphere while the detector is on the outside. An advantageous method according to the invention is a method wherein a gas sensor as described
10 above is present on the inside of the package while the sensor can be read out from the outside by a detector. This makes it a non-invasive measurement method. The advantage is that there is no need to open the package for quality control.

By the choice of the sensing material it is possible to measure the level of all kinds of gases inside the package as long as the sensing material is
15 responsive to the gas that should be determined. For example when the level of oxygen inside the package should be determined, the sensing material should be chosen so as to be able to react in some way or another to the presence of oxygen. When for example bacterial spoilage of a food product should be determined, a sensing material should be chosen that is able to react in some way to a gas that is
20 produced by the bacteria when present on the food product. Examples of gases that are produced by bacteria when present on a food product are putrescine, cadaverine, histamine, spermidine, tyramine or other volatile compounds such as ammonia, trimethylamine, acetic acid, hydrogen sulfide and aldehyde compounds. The above-mentioned gases can also change the pH of the environment; this change can also be
25 detected with a fluorescent dye which changes in characteristics upon exposure to differences in pH.

Examples of gases inside the package that are worthwhile monitoring or measuring are for example oxygen, carbon dioxide, ammonia and ethylene. Sometimes, with the right choice of sensing material it will be possible to measure or
30 monitor more than one type of gas by the use of one type of sensing material. It appeared advantageous to be able to monitor the oxygen or carbon dioxide level inside the package. It was found especially advantageous to be able to monitor oxygen and carbon dioxide with the same sensing material.

Oxygen and/or carbon dioxide are gases that are very relevant for the
35 quality of packaged food and beverages. Examples of food and beverages are meat,

poultry, fish, dairy products, vegetables and fruits. Examples of vegetables are broccoli, cauliflower, potatoes, lettuce, leeks, Brussels sprouts, beans, cabbage, celery, tomato, artichoke, radish, parsley and spinach. Examples of fruits are bananas, strawberries, blackberry, blueberry, cherry, fig, apples, pears, pineapple, mango, papaya, cranberry, plum, grape and citrus fruit such as for example orange, mandarin, lemon, lime and grape fruit. Examples of meat and poultry are beef, lamb, horse, goat, pig, sheep, rabbit, turkey, chicken, duck, and goose. Examples of fish are shrimps, salmon, mackerel, haddock, herring, squid, tuna, shark, swordfish, lobster, oyster, tilapia, anchovies, catfish, cod, mullet, sardine and snapper. Examples of dairy products are butter, cheese, ice cream, milk and yoghurt.

It is advantageous to use in packaged meat, poultry, fish or dairy products a sensor according to the present invention that is able to react to the presence of ammonia and/or biogenic amines. Next to being advantageous for food and beverages, it can also be relevant for packaged seeds and fresh flowers to measure and/or monitor the atmosphere inside the package.

Suitable materials to act as sensing material in the gas sensor according to the invention are fluorescent materials. Fluorescent materials absorb light in a certain region of the spectrum and fluoresce in another region of the spectrum. The presence of a gas, such as for example oxygen or carbon dioxide, quenches the fluorescent light from the fluorescent material. The more of a certain gas is present, the more the fluorescent light is quenched. Another type of fluorescent dye reacts with the gases of interest and upon this reaction the dye gets fluorescent characteristics or alternatively loses its fluorescent properties. The amount of fluorescence or loss of fluorescence characteristics is characteristic for the amount of gas reacted with the applied dye.

By all these mechanisms it is possible to use fluorescent light that reaches a suitable detector to determine the concentration of the gas present inside the package. Examples of fluorescent materials are ruthenium (Ru) complex, osmium (Os) complex, platinum (Pt) complex, Iridium (Ir) complex, Rhenium (Re) complex, Rhodium (Rh) complex, polycyclic aromatic hydrocarbons, metalloporphyrines, C60- or C70- fullerene or a combination of any of them. Examples of polycyclic aromatic hydrocarbons are pyrene, 1-pyrene decanoic acid, 1-pyrene dodecanoic acid perfluorodecanoic acid or 1-decyl-4-(1-pyrenyl)butanoate. Examples of metalloporphyrines are (Pt²⁺, Pd²⁺, or Zn²⁺-) metalloporphyrines. Preferred fluorescent materials are chosen from the list (Ru)- complex, (Pt)- complex, (Pd)- complex or a

combination of any of them. More preferred fluorescent materials are tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride, tris(2,2'-bipyridyl)ruthenium(II), tris(1,10-phenanthroline)ruthenium(II) dichloride, platinum(II)-octaethylporphine-ketone, platinum(II)-tetraphenylporphyrin, palladium(II)-tetraphenylporphyrin and combinations
5 of any of them.

Examples of fluorescent dyes detecting other species such as amines, thiol compounds, aldehyde compounds, are mentioned in literature. Reference is for example made to: "Handbook of derivatization reactions for HPLC", G. Lunn and L.C. Hellwig (Eds.), John Wiley & Sons Inc., 1998 or "The Handbook: A Guide to
10 Fluorescent Probes and Labeling Technologies", R.P. Haugland (Ed.), 10th Ed., Invitrogen/Molecular Probes; Carlsbad, CA, 2005.

The fluorescent light can be detected amongst others by commercially available apparatus, such as for example O₂xySense fluorescence apparatus of OxySense®, Dallas, USA.

15 An advantage of a gas sensor comprising a fluorescent sensing material is that a short response time can be reached. With response time is meant the time between a certain change in the relevant gas composition and the time the gas sensing material reacts to that change. Preferably response times of less than 25 seconds are possible, more preferably gas sensors with a maximum response time of
20 10 seconds are used.

An additional advantage of a gas sensor comprising a fluorescent sensing material is that by the nature of the fluorescent sensing material it will not be "consumed" when a gas is sensed. Whether the fluorescent gas sensor senses the gas one, ten or hundred times or even more, the gas sensing material will each time be
25 available for a next indication. This makes it possible to handle the sensor without special precautions, such as would be necessary when one would use a color indicating sensor. A color indicating sensor is active only once and thus when the sensor is sensitive to oxygen, special precautions have to be taken to keep oxygen away from the sensor until it is required to detect oxygen. This means that when a
30 color- indicating oxygen sensor is going to be used in a package with fresh meat for example, it is necessary to keep the sensor isolated from the surrounding atmosphere until the package is closed and the sensing must start. This requires special handling and packaging instructions and conditions to prevent the gas sensor from being active in a too early stage.

A further advantage of a gas sensor comprising a fluorescent sensing material is that it gives a momentary indication whereby the sensing material is not used-up or consumed. This implies that the sensor can be used over and over again. Each time the sensor is irradiated the measurement can be performed. This is contrary
5 to for example a color- indicating sensor where the change in color is initiated by a reaction between the dye and the gas to be determined. Thus as soon as the concentration of the relevant gas close to the color-indicating sensor, is high enough to initiate the reaction, the sensor changes irrevocably its color, thereby more or less “consuming” the sensor. Therefore the sensor is not available anymore for sensing at a
10 later point in time.

Another advantage of a gas sensor comprising a fluorescent sensing material is that it gives the required indication only on request. That is it doesn't spoil the esthetical appearance of the sometimes carefully designed packaging material. A color indicating sensing material at least changes the appearance of the packaging
15 material irreversibly. Therefore the consumer or user of the packaged material gets another impression of the packaged material.

The gas sensor according to the present invention comprises at least one sensing material. It is within the scope of the present invention to combine two or more sensing materials and incorporate them into one substrate. This can be
20 advantageous when more than one type of gas needs to be sensed.

For the gas to reach the sensing material that is embedded in the substrate, it is necessary that the substrate is made out of a polymeric material that has high gas permeability. When the gas permeability is too low it will take too long for the gas to reach the sensing material and thus the response time of the sensing material to
25 the (changes in the concentration of the) gas will become too long. Therefore to have a quick response time the permeability of the polymeric material must be sufficiently high. One skilled in the art will of course understand that when the sensing material is chosen to measure and/or monitor for example oxygen the permeability of the polymeric material for oxygen should be sufficient high.

30 A suitable polymeric material as substrate for a sensing material has at least the gas permeability relevant for the gas to be sensed:

1. gas permeability for O₂ of at least 200 cm³.mm/(m².day.atm) at 23 °C and 0% relative humidity (RH)
2. gas permeability for CO₂ of at least 1000 cm³.mm/(m².day.atm) at 23 °C and
35 0% RH

3. gas permeability for NH_3 of at least $50 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 23°C and 0% RH

With "the property relevant for the gas to be sensed" is meant that the gas to be determined dictates the requirements for the substrate. Thus when the gas to be sensed is oxygen then the relevant property referred to is the permeability for oxygen; when the gas to be sensed is CO_2 , then the relevant property referred to is the permeability for CO_2 .

A suitable polymeric material as substrate for an oxygen sensing material has a gas permeability for O_2 of at least 200 and preferably at least 400 $\text{cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 23°C and 0% relative humidity (RH). A suitable polymeric material as substrate for a carbon dioxide sensing material has a gas permeability for CO_2 of at least 1000, preferably at least 1500 $\text{cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 23°C and 0% RH. A suitable polymeric material as substrate for an ammonia or biogenic amine sensing material has a gas permeability for NH_3 of at least $50 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 23°C and 0% relative humidity (RH), preferably at least $100 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 23°C and 0% relative humidity (RH). It is preferred to use polymeric materials that have the combination of gas permeability for O_2 of at least $200 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ and gas permeability for CO_2 of at least $1000 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ both determined at 23°C and 0% RH. It is even more preferred to use polymeric materials that have the combination of gas permeability for O_2 of at least $200 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$, gas permeability for CO_2 of at least $1000 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ and gas permeability for NH_3 of at least $50 \text{ cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ all determined at 23°C and 0% RH.

The gas sensors according to the present invention have properties that make them suitable for use in the packaging industry. The substrate of the gas sensor is made out of a polymeric material which is suitable for film melt processing. It was found that by using such a substrate the gas sensor according to the invention can easily be used in the industrial packaging processes and that the packaging process can still be executed on generally used packaging machines. In the packaging industry huge packaging machines are used to package all kinds of materials at high speed. Examples in this field are filling of bottles, pouches and trays, for example for convenient foods such as ready-to-cook meals. Other examples are packaging of fresh cut vegetables and fruits. Because of the nature of the materials to be packaged and the huge amounts to be packaged, the machines operate at very high speeds. Another advantage of such a film melt processable polymeric substrate is that the gas sensor can rather easily be incorporated into the rest of the packaging material. The invention

also relates to a packaging material comprising a gas sensor according to the invention.

One of the most often used base packaging concepts is starting from film material. The film can be used as such or it can be post-formed for example by vacuum forming or lamination into multilayers. Polymeric materials that are suitable as substrate in the gas sensor according to the invention, whether used as film or in another form, are film melt processable. Preferred polymeric materials suitable as substrate have a zero shear rate melt viscosity at a temperature of 40 °C above its melting temperature of at least 100 Pa.s, preferably at least 500 Pa.s, more preferably at least 1200 Pa.s according to the capillary viscosity measurement as described in ISO 11443. The melting temperature of the material can be determined by a differential scanning calorimetry method as described in ISO 11357-3.

Preferred polymeric materials suitable as substrate are not chemically crosslinked. It was found that this makes them easier to handle in high-speed processing apparatus. More preferred polymeric materials suitable as substrate are not chemically crosslinked and have a zero shear rate melt viscosity at a temperature of 40 °C above its melting temperature of at least 100 Pa.s, preferably at least 500 Pa.s, more preferably at least 1200 Pa.s.

Suitable examples of polymeric materials that can be used as substrate in the present invention are polyethylene, polypropylene, ethylene-propylene copolymers, ethylene vinyl acetate copolymer (EVA), polyvinyl alcohol, fluoro-containing polymers, polyamide, polyester, polyurethane, polyether, polyesteramide and blends or copolymers of any of them. Further suitable polymeric materials are blockcopolymers based on two types of blocks: crystallisable blocks such as for example based on polyester (e.g. PBT or PET) or polyamides (e.g. PA6, PA11, PA12) and (at room temperature) amorphous blocks based on polyethers (e.g. PPG, PEO, PTHF) or polysiloxanes. Preferred materials are blockcopolymers based on PBT as hard block and polyethers as soft block, such as PEO and PPG. More preferred materials are Arnitel® VT 3104 and Arnitel® VT 3108 sold by DSM Engineering Plastics, NL. Most preferably Arnitel® VT 3104, is used because of its advantageous combination of properties.

Sometimes gas sensors are described that are based on a luminophore and a sol-gel matrix as in WO2004/077035. This kind of systems is however much more difficult to make and handle because of the elaborate process of preparing a sol-gel matrix. This makes the whole production process and the sensor

much more expensive and therefore unsuitable for industrial processes such as in the packaging industry.

The gas sensors according to the present invention are preferably non-porous as that makes them easier to prepare and handle in further processing steps. Additionally these materials are less expensive.

It is possible that the combination of the sensing material with the substrate material gives rise to coloration of the composition. This is however not detrimental to the gas sensing method, as long as the fluorescent light can reach an on the outside located detector. Preferably the polymeric material that makes up the substrate is transparent, semi-transparent or translucent. More preferably the polymeric material is transparent.

The invention also relates to a packaging material comprising a gas sensor as described above. The packaging material according to the present invention can be fully made out of the gas sensor according to the invention and can thus be used as a packaging material as such. However it is also very well possible that the packaging material according to the invention is only partially made out of the gas sensor according to the invention; thus for example the packaging material contains only in a relatively small area a gas sensor. Even when the gas sensor only makes up a part of the packaging it will be able to function reliably as a gas sensor. In such an arrangement it is advantageous to incorporate the gas sensor into a material that has the function to cover or pack the article.

The size of the gas sensor is not particularly critical as long as it can be combined with the rest of the packaging material and as long as the signal from and to the, on the outside located, detector can be effectively determined. The shape of the gas sensor, when used as only a part of the packaging material is not particularly critical. In the embodiment where the gas sensor makes up only a part of the packaging material, it is preferred to use the gas sensor in the form of a strip. In such a case the gas sensor is used as a layer with a smaller width than the other layers. The gas sensor can then be considered a strip for example placed between 2 or more layers. It is advantageous to use it in a strip as the strip can easily be integrated during the packaging process. It can namely be integrated continuously during the process of making packaging materials or during the packaging process itself.

The invention also relates to a single- or multi- layer packaging concept wherein at least one of the layers comprises a packaging material according to the invention. As described above, the packaging material can be fully or partially made

out of the gas sensor according to the invention. In a multilayer packaging concept more than one, preferably at least 3 layers are used. Advantageously it is applied in a multi-layer concept as in such a concept the material for each layer can be chosen optimally as less optimal properties in one layer can be compensated in another layer,
5 resulting in the best packaging material.

In a multilayer packaging concept according to the invention at least one of the layers comprises a packaging material according to the invention, optionally combined with one or more other layers. In such a multilayer arrangement several layers are combined, each with its own properties and thus advantages. It makes it
10 therefore possible to combine for example a layer with a high permeability for oxygen with other layers that are less permeable for oxygen or behave as a barrier layer for a certain gas. Or it is possible to use as an outer layer a layer that is very suitable for printing information text on. In this multilayer concept it is also possible to use one or more tie layers that have the function to tie several layers to each other, this can be
15 advantageous or sometimes even necessary when certain layers in the multilayer concept would not, or not sufficiently, adhere to each other. The man skilled in the art of multilayer packaging materials knows or can easily determine which combination of layers is advantageous or necessary for each use. The separate layers in the multilayer concept need not have the same dimensions. For example the thickness and
20 the width can be different for the various layers.

In the multilayer packaging concept according to the invention the layer with the gas sensor is advantageously protected against for example mechanical impact by one or more layers. Generally the layer with the sensing material will be arranged to be closest to the inside of the package as the gas concentration in the
25 inside of the package is the most relevant concentration to determine. For example when the material in the package is fruit such as for example bananas, it can be relevant to determine the level of oxygen and/or carbon dioxide close to the bananas and thus in the inside of the package. Thus the gas sensor will be located as close as possible to the inside of the package. More to the outside of the package, in this
30 exemplary arrangement, layers will be present that are less permeable to oxygen than the polymeric material in the gas sensor, so as to prevent oxygen from entering the package. These layers that are located more to the outside of the package will in this arrangement preferably have oxygen barrier properties.

The gas sensor according to the invention can advantageously be
35 combined with one or more layers made out of a barrier material. The barrier material

will prevent a certain gas to enter into the package. A specific barrier material will generally behave as a barrier for certain gases but possibly not for all gases. Therefore when the gas sensor that is present in the package is selected to react to, for example, oxygen, generally an oxygen- barrier layer will be used in the construction of the packaging material, when the gas sensor is selected to react to another gas, generally a barrier layer for that gas will be used in the construction of the packaging material. Suitable materials for use as barrier layer for oxygen and/ or carbon dioxide are polyamide, polyester, polyethylene vinyl alcohol, polyvinylidene chloride.

In one embodiment of the invention the sensing material is distributed through the bulk of the polymeric material that functions as the substrate for the sensing material. This can be homogeneously distributed or inhomogeneously. An inhomogeneous distribution can be random or spatially confined.

The invention also relates to the use of a single- or multi-layer packaging concept according to the present invention for packaging a product. Using the packaging concept according to the invention with an incorporated gas sensor is advantageous as by the presence of the gas sensor, it is possible to detect immediately whether the packaged product inside the package has still a good quality. As the gas sensor works together with the detector in a non-invasive manner, the package stays intact and thus when the quality is still sufficient no new packaging need to be applied. A new packaging would be required when first the package of the product had to be opened to determine the quality by traditional detection methods. Thus the use of the non-invasive detection system reduces the amount of packaging material and thus the costs and later-on waste; additionally the quality can be determined at any time.

The invention also relates to the use of a packaging material comprising a gas sensor according to the present invention for packaging a food product. Using the packaging material according to the invention in food applications is advantageous as it could be detrimental to the quality of the food product when the packaging should first be opened to be able to determine the quality. Repackaging the food product is almost impossible as a high risk exists to, for example, bacterial spoilage or spoilage by other food contaminants. Therefore determining the quality of a packaged food product almost always leads to throwing away the tested food product. This method of (invasive) testing thus results in a loss of food products that could be sold for consumption and thus this method increases the amount of waste.

The invention further relates to a process for preparing a gas sensor according to the present invention wherein the process comprises at least the following steps: melting the polymeric material, blending the sensing material and the polymeric material and shaping the melt into its desired form by a melt processing step.

- 5 Depending on the nature of the sensing material and the polymer, the step of melting and blending can be interchanged or combined into one step. Depending on the required arrangement of the sensing material in the polymeric material the blending can be throughout the bulk of the polymeric material or the sensing material can be located in a narrowly defined area, for example by the use of an injection nozzle to add
10 the sensing material.

- The invention also relates to a non-invasive method to determine the quality of a packaged product whereby the quality of the packaged product is determined based on the composition of the atmosphere surrounding the packaged product inside the package which composition is determined with a detector that is
15 placed on the outside of the package and a gas sensor according to the invention that is incorporated into the packaging material and that is placed on the inside of the package. With a gas sensor that is incorporated into the packaging material the method can be easily applied as there is no possibility that objects get into the way between the detector and the sensor. An additional advantage with an incorporated sensor is that
20 when the quality control is performed automatically, for example in a packaging line or during transport, it is almost a requirement that the gas sensor should be at a fixed location because else the detector will be in the wrong position with respect to the gas sensor.

- The invention will be elucidated with reference to the following, non-
25 limiting examples.

Example I: Preparation of oxygen sensitive gas sensors with as matrixes polymers with different block-co-polyether-esters

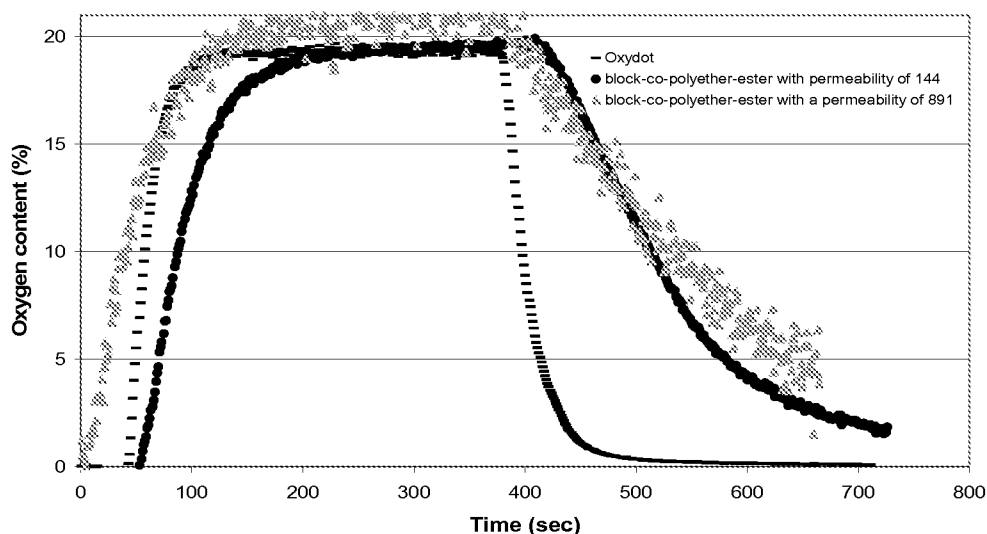
- Two types of block-co-polyether-ester grades were applied (PEE1
30 and PEE2). PEE1 consists of 65 wt% butyleneterephthalate and 35 wt% ethyleneoxide blocks. PEE2 is based on 45 wt% butyleneterephthalate and 55 wt% (ethyleneoxide – propyleneoxide – ethyleneoxide) triblocks with corresponding oxygen permeability of 144 and 891 cm³.mm/(m².day. atm) at 23 °C and 0 % RH. Each grade was powder mixed with 0.077 (w/w) % of tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II)
35 dichloride complex (CAS number: 36309883). This powder mixture was added to a

conical co-rotating fully intermeshing lab-scale twin-screw extruder in order to melt mix the Ru-complex with the polymer.

The mixing was carried out at a barrel temperature of 230 °C, a rotation speed of 120 rpm and a residence time of 3 minutes. The experiments were carried out under nitrogen flush. The resulting materials were pressed between flat hot plates into films with a thickness of approximately 70 micrometer. The dimensions of the films were 10*10 cm². Pressing conditions were: plates temperature: 230°C, time between plates without pressure: 3 min, subsequently pressurizing the system for 3 minutes at 10kN, subsequently pressurizing the system for 3 min at 50 kN and subsequently pressurizing the system at 180 kN and start the cooling until room temperature.

The oxygen response curve of a gas sensor that is commercially available under the name O₂xyDot™ of OxySense®, USA, was measured and compared with the different block-co-polyether-ester grades films containing the ruthenium complex incorporated. The O₂xyDot™ gas sensor is based on an oxygen sensitive coating immobilized in a porous membrane.

The measurements were performed in a glass tube containing the O₂xyDot™ or the different block-co-polyether-ester grade films. The atmosphere in this glass tube can be controlled by a flow meter and can be changed between oxygen and nitrogen. This allows monitoring the oxygen time response curve upon increasing oxygen concentrations (between 0 % and 21 %). The measurements were performed with a commercial available O₂xySense fluorescence apparatus of OxySense®, USA.



From the results it can be concluded that the two block-co-polyether-ester grades with an incorporated gas sensing material show a good response to oxygen and are therefore able to function as good and easy-to-produce gas sensors.

CLAIMS

1. Gas sensor comprising at least one sensing material embedded in a substrate wherein the sensing material is a fluorescent material and the substrate is
5 made out of a polymeric material that is suitable for film melt processing and has high gas permeability
2. Gas sensor according to claim 1 characterized in that the polymeric material has at least the gas permeability relevant for the gas to be sensed:
 - a. gas permeability for O₂ of at least 200 cm³.mm/(m².day.atm) at 23 °C and
10 0% relative humidity (RH)
 - b. gas permeability for CO₂ of at least 1000 cm³.mm/(m².day.atm) at 23 °C and 0% RH
 - c. gas permeability for NH₃ of at least 50 cm³.mm/(m².day.atm) at 23 °C and 0% RH
- 15 3. Gas sensor according to claim 1 or 2 characterized in that the sensor is suitable for detecting oxygen (O₂) and/or carbon dioxide (CO₂)
4. Gas sensor according to anyone of claim 1-3 characterized in that the sensor is suitable for detecting NH₃ and/or biogenic amine
5. Gas sensor according to anyone of claim 1-4 characterized in that the
20 polymeric material has a zero shear rate melt viscosity at a temperature of 40 °C above its melting temperature of at least 100 Pa.s
6. Packaging material comprising a gas sensor according to anyone of claim 1-5
7. Packaging material according to claim 6 characterized in that the packaging material is only partially made out of the gas sensor and that the gas sensor is
25 used in the form of a strip
8. Single- or multi- layer packaging concept wherein at least one of the layers comprises a packaging material according to claim 6 or 7
9. Use of a single- or multi-layer packaging concept according to claim 8 for packaging a product
- 30 10. Process for preparing a gas sensor according to anyone of claim 1-5 wherein the process comprises at least the following steps: melting the polymeric material, blending the sensing material and the polymeric material and shaping the melt into its desired form by a melt processing step
11. Non-invasive method to determine the quality of a packaged product whereby
35 the quality of the packaged product is determined based on the composition of

the atmosphere surrounding the packaged product inside the package which composition is determined with a detector that is placed on the outside of the package and a gas sensor according to anyone of claim 1-5 that is incorporated into the packaging material and that is placed on the inside of the package

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/051460

A. CLASSIFICATION OF SUBJECT MATTER

INV. G01N31/22

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)
G01N

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 practical, 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 99/59431 A (THOMAS J HORAN FAMILY TRUST [US]; STOLTENBERG HERBERT W [US]; STOLTENB) 25 November 1999 (1999-11-25) pages 2-7 -----	1-3,5-11
X	WO 2004/077035 A (GAS SENSORS SOLUTIONS LTD [IE]; MCEVOY AISLING [IE]; MACCRAITH BRIAN []) 10 September 2004 (2004-09-10) page 3, last paragraph - page 6 -----	1-3,5,10
X	WO 2004/031321 A (NAT RES COUNCIL [CA]; UNIV CARLETON [CA]; EVANS CHRISTOPHER EDWARD BRI) 15 April 2004 (2004-04-15) page 7, line 4 - page 8, line 11 page 12, line 5 - page 16, line 9; table 1 ----- -/--	1-3,5,10

☒ 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 document 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.
- *8* document member of the same patent family

Date of the actual completion of the international search

9 May 2008

Date of mailing of the international search report

24/07/2008

Name and mailing address of the ISA/

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Authorized officer

Michalitsch, Richard

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/051460

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/019179 A (3M INNOVATIVE PROPERTIES CO [US]) 6 March 2003 (2003-03-06) page 6, line 27 - page 8, line 20 page 15, line 17 - page 18, line 21	1-3,5, 10,11
X	EP 1 598 667 A (POWDERTECH CO LTD [JP]) 23 November 2005 (2005-11-23) paragraphs [0022] - [0026] paragraph [0035] paragraph [0038] paragraph [0048] paragraphs [0078], [0079]	1,3,5,10
X	WO 99/09406 A (NOVARTIS AG [CH]; NOVARTIS ERFIND VERWALT GMBH [AT]; WALDNER ADRIAN [C]) 25 February 1999 (1999-02-25) page 1 - page 3, paragraph 1 page 8, paragraphs 3,4	1-3,5,10
X	WO 99/37998 A (BAYER AG [US]; BERGER JOSEPH [CH]; COLLINS THOMAS C [US]; SLOVACEK RUD) 29 July 1999 (1999-07-29) abstract page 5, lines 15-30 page 6, lines 1-15 page 7, line 23 - page 8, line 8 page 9, lines 1-11 examples 2,3	1-3,5, 10,11
X	EP 0 109 958 A (AVL AG [CH]) 30 May 1984 (1984-05-30) pages 3,4	1-3
X	US 2004/171094 A1 (KLIMANT INGO [DE] ET AL) 2 September 2004 (2004-09-02) page 3, last paragraph - page 6	1-3
X	US 5 173 432 A (LEFKOWITZ STEVEN M [US] ET AL) 22 December 1992 (1992-12-22) figure 1 column 1, lines 63-68 column 4, lines 20-40	1-3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2008/051460

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1, 2 (in part), 3, 5-11 (in part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1,2 (in part), 3, 5-11 (in part)

Oxygen or carbondioxide gas sensor based on a fluorescent sensing material embedded in a gas permeable polymeric substrate.

2. claims: 1,2 (in part), 4, 5-11 (in part)

Ammonia or biogenic amine gas sensor based on a fluorescent sensing material embedded in a gas permeable polymeric substrate.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/051460

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9959431	A	25-11-1999	AU 3987199 A CA 2330646 A1 US 6149952 A	06-12-1999 25-11-1999 21-11-2000
WO 2004077035	A	10-09-2004	AU 2004215131 A1 CA 2517071 A1 EP 1597563 A1 IE 20030144 A1 JP 2006519381 T US 2006257094 A1	10-09-2004 10-09-2004 23-11-2005 08-09-2004 24-08-2006 16-11-2006
WO 2004031321	A	15-04-2004	AU 2002328731 A1	23-04-2004
WO 03019179	A	06-03-2003	EP 1423691 A1 JP 2005501256 T US 2003099574 A1	02-06-2004 13-01-2005 29-05-2003
EP 1598667	A	23-11-2005	AU 2004215093 A1 JP 2004254684 A WO 2004077049 A1 KR 20050096972 A US 2006141106 A1	10-09-2004 16-09-2004 10-09-2004 06-10-2005 29-06-2006
WO 9909406	A	25-02-1999	AT 294387 T AU 9262698 A DE 69829977 D1 DE 69829977 T2 JP 2001516026 T US 6338822 B1	15-05-2005 08-03-1999 02-06-2005 06-10-2005 25-09-2001 15-01-2002
WO 9937998	A	29-07-1999	AU 1778199 A CA 2318950 A1 EP 1049924 A1 JP 2002501192 T US 6190612 B1	09-08-1999 29-07-1999 08-11-2000 15-01-2002 20-02-2001
EP 0109958	A	30-05-1984	AT 379688 B DE 3375826 D1 JP 1821979 C JP 5032701 B JP 59108957 A US 4587101 A	10-02-1986 07-04-1988 10-02-1994 17-05-1993 23-06-1984 06-05-1986
US 2004171094	A1	02-09-2004	NONE	
US 5173432	A	22-12-1992	NONE	