



(43) International Publication Date
22 November 2012 (22.11.2012)

(51) International Patent Classification:
F25D 17/04 (2006.01)

(21) International Application Number:
PCT/EP2012/055778

(22) International Filing Date:
30 March 2012 (30.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11166614.5 18 May 2011 (18.05.2011) EP

(71) Applicants (for all designated States except US): **WHIRLPOOL CORPORATION** [US/US]; 2000 M 63, Benton Harbor, MI 49022 (US). **GOODEN, Corey**; V.le G. Borghi 27, I-21025 Comerio (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BIOTTI, Carolina** [IT/IT]; V.le G. Borghi 27, I-21025 Comerio (IT). **SOTO, Cristian**; V.le G. Borghi 27, I-21025 Comerio (IT).

(74) Agent: **GUERCI, Alessandro**; V.le G. Borghi 27, I-21025 Comerio (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FRUITS AND VEGETABLES COMPARTMENT OF A REFRIGERATOR WITH MEANS FOR PRESERVING FRESHNESS

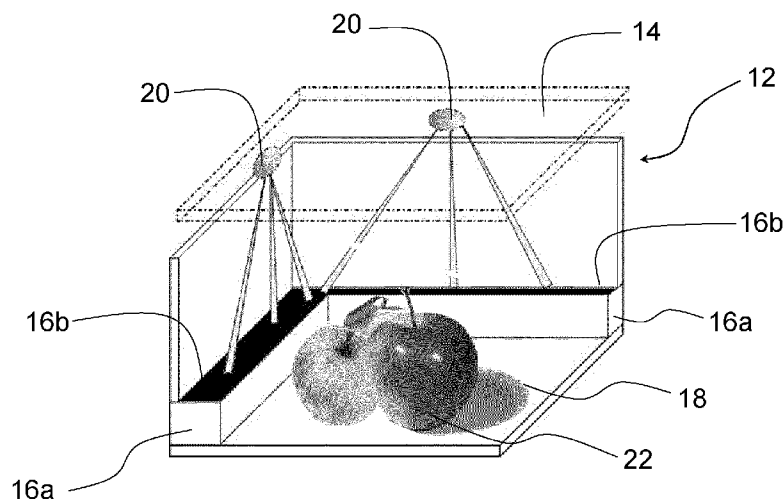


Fig. 1D

(57) Abstract: It is disclosed a compartment (10) of a refrigerator for storage of fruits and vegetables provided with a photo-catalytic element (16) combined with an array of UV lamps (20) that promote the conversion of ethylene released by fruits and vegetables to carbon dioxide and water. The ripening process is thus controlled by both removing ethylene and producing carbon dioxide, whereby the freshness of fruits and vegetables is extended and/or preserved.



FRUITS AND VEGETABLES COMPARTMENT OF A REFRIGERATOR WITH MEANS FOR PRESERVING FRESHNESS

The present invention relates to a compartment of a refrigerator for storage of fruits and vegetables provided with means for preserving freshness. More particularly, the invention relates to a compartment of a refrigerator provided with means for controlling the ripening process and extending or preserving the freshness of fruits and vegetables by modifying the atmosphere within the compartment via a photo-catalytic process.

Refrigerators typically have special compartments, or "crisper drawers", to store fruits and vegetables, sometimes with mechanisms to control the humidity in the drawer.

Many vegetables are sensitive to ethylene, a chemical released by many fruits and some vegetables. In general, fruits release more ethylene than vegetables in the natural ripening process. Foods that emit ethylene include: apples, avocados, bananas, pears, peaches, plums, cantaloupes, honey dew melons, mushrooms, and tomatoes. Vegetables that absorb ethylene include: brassicas, leafy greens, beans, carrots, cucumbers, eggplant, peas, peppers, and potatoes.

In general, ethylene increases the ripening process of fruits and vegetables. Such process includes a degradation of complex insoluble carbohydrates to simple soluble sugar compounds (e.g. glucose, fructose), which in turn cause an increasing in the sweetness and a loss of consistency of the foodstuff. The overall result is reduction of freshness and of shelf life.

As fruits and vegetables ripen in the closed compartment of a refrigerator, ethylene is released and accumulated in the atmosphere of the closed compartment, which accelerates the ripening process of the surrounding produce, thereby reducing the shelf life and the freshness of the produce.

Since ethylene is physiologically active in traces (0.1ppm), it would be desirable to separate produces that are sensitive to ethylene from those releasing large amounts of such gas, and store them in separate and spaced-apart compartments. This, however, may not be a viable option due to the limited space available in a refrigerator.

The ripening process could be slowed down by reducing oxygen or ethylene content and/or increasing the concentration of inhibitor gases such as carbon dioxide.

U.S. 5,253,448 discloses a vegetables storage drawer of a refrigerator equipped with a gas-absorbing member disposed over the drawer to absorb noxious gases emitted by the vegetables. The absorbing member is a plate shaped from a traditional zeolite powder and is placed under a UV lamp that is switched on and off according to a predetermined time sequence. When the lamp is on, the absorbing member saturated with the noxious gases is regenerated, namely it turns to unsaturated and is ready to absorb noxious gases again.

The refrigerator storage drawer described above is based on the absorption of gases, including ethylene, by a zeolite material. It is not disclosed, however, what is the zeolite regeneration process, in particular it is not disclosed whether the absorbed gases are re-emitted into the drawer, which would not solve the problem, or are transformed into other substances.

Japanese patent publication JP 72-70044A discloses a gas removing device for a vegetable storage drawer of a refrigerator. The device includes an optical catalyst such as titanium or zinc oxide and an ultraviolet lamp. This latter activates the catalyst which decomposes ethylene or other ripening agents or substances causing bad smell. The gas removing device is confined in the ceiling of the

vegetable storage drawer and comprises an elongated UV lamp (26) surrounded by the catalytic element (25) separated from the storage drawer by a perforated plate (29). The shape and size of the catalytic element, however, do not seem to be such as to provide a maximum contact area with the air in the drawer, which would be required to ensure an optimal catalytic efficiency. The only active part in controlling ripening is directly related to the lighting system and not to gases associated with the system itself. Also, the device is not designed to optimize the contact of the air containing the undesired gases with the catalytic surface since a protective cover consisting of a perforated plate is placed between the device and the storage compartment. Also, mounting of the device within the refrigerator requires certain modifications of the typical structure of the refrigerator inner parts. Therefore the effectiveness of this device is in doubt.

There remain, thus, several disadvantages to, or problems not solved by, the vegetables storage drawers disclosed in the prior art documents mentioned above. There is a need, therefore, for a fruit and vegetable compartment of a refrigerator that efficiently and effectively removes undesired ripening substances released by fruits and vegetable, thereby extending the shelf-life and freshness of such produces in a cost-effective way and minimizing the modifications to be made to the structure of the refrigerator.

It is therefore the overall object of the present invention to disclose an improved fruit and vegetable compartment of a refrigerator capable of controlling the ripening process of fruits and vegetables by preventing or limiting undesired and/or exceedingly fast ripening.

It is a further object of the present invention to disclose an improved fruit and vegetable compartment of a refrigerator capable of removing ethylene released

during the ripening process of fruits and vegetables and converting it into substances that do not accelerate or limit the ripening process of fruits and vegetables.

It is a still further object of the present invention to disclose an improved fruit and vegetable compartment of a refrigerator which is cost-effective both during the manufacturing process and when functioning during the entire life of the refrigerator.

The present invention addresses these needs by providing a compartment of a refrigerator for storage of fruits and vegetables comprising a photo-catalytic element and a source of UV light, said compartment comprising a bottom and an open upper part defining an inner chamber open upwards, said compartment being characterized in that:

- said photo-catalytic element is housed on the bottom of said inner chamber of said compartment or is mounted directly above said inner chamber, said photo-catalytic element comprising at least a portion extending along or being superimposed to the peripheral portion of the bottom of said chamber; and
- said source of UV light comprises a plurality of UV lamps arranged above said photo-catalytic element, so that the UV light emitted by said lamps hits directly said photo-catalytic element.

More particularly, the invention relates to a compartment of a refrigerator for storage of fruits and vegetables provided with means for controlling the ripening process and extending or preserving the freshness of fruits and vegetables by modifying the atmosphere within the compartment via a photo-catalytic process that converts ethylene into carbon dioxide and water.

Volatile organic compounds (VOC) present in the air at low concentrations can be oxidized to carbon dioxide and water when exposed to particles of titanium dioxide irradiated with near UV light. Suitable titanium dioxide particles are produced from titanium dioxide-sol generated by controlled hydrolysis of titanium isopropoxide. Titanium dioxide particles supported on suitable supports exhibit higher photo-catalytic activity than unsupported titanium dioxide pellets.

The photo-assisted catalytic degradation of ethylene carried out by means of photo-reactors packed with TiO_2 pellets prepared by sol-gel method is described in the literature. The reaction rate depends on the on the light intensity, feed composition (ethylene, oxygen and water vapour) and temperature. It is reported that more than 95% ethylene was always completely mineralized irrespective of the reaction conditions.

It is known to a skilled person that other oxides of transition metals exert a photo-catalytic action in the conversion of ethylene or other VOC to carbon dioxide and water. Zinc oxide is an example of such photo-catalytic transition metals oxides.

According to an aspect of the present invention, a refrigerator having a fruits and vegetable compartment is provided with means to carry out a photo-assisted catalytic degradation of ethylene and other VOC present in the atmosphere of the refrigerator.

According to another aspect of the present invention, the carbon dioxide produced by the reaction of ethylene and VOC conversion is substantially confined within the compartment and kept in contact with the produces contained therein, so that such carbon dioxide exerts an inhibitory effect of the ripening process of such produces.

Therefore, according to an aspect of the present invention a photo-catalytic element is directly housed in the fruits and vegetables compartment of the refrigerator or is mounted directly above said compartment without any protective cover or other parts interposed between the catalytic element and the fruits and vegetables stored in the compartment. This serves the twofold function of maximising the contact between the ethylene/air mixture contained in the compartment and the photo-catalytic element to promote the conversion of ethylene to carbon dioxide, and maximise the contact of the carbon dioxide so produced with the fruits and vegetable, whereby the ripening process is inhibited or prevented.

According to an aspect of the present invention the photo-catalytic element comprises a support and an amount of TiO_2 particles of from 2 to 30% by weight, preferably from 5 to 20% by weight, more preferably from 8 to 15% by weight.

According to another aspect of the invention the photo-catalytic element comprises TiO_2 particles having an average size of from 0.1 to 20 μm , preferably from 0.5 to 15 μm , more preferably from 1 to 10 μm . Preferably the TiO_2 particles are in the anatase polymorphic form.

According to an embodiment of the invention the photo-catalytic element comprises a polymeric film coated with TiO_2 particles obtained by applying a layer of a suspension of TiO_2 particles in a suitable dispersing medium.

For example, a titanium dioxide-coated food packaging film prepared by using a colloidal suspension of anatase TiO_2 was tested for its catalytic properties towards the photo-degradation of ethylene. The TiO_2 suspensions were coated onto the surface of oriented-polypropylene film (OPP) using a bar coater and dried in air. The resulting film had a milky whitish appearance and it was found that the

ethylene decomposition rate increased as the TiO_2 particle size was within the ranges defined above. An excellent photo-catalytic activity was obtained with the 10% TiO_2 particles coated film. The reduction of ethylene in the compartment atmosphere achieved by TiO_2 -coated film was of about 90% using UV light lamps. According to another embodiment of the invention the catalytic element comprises a fabric or nonwoven impregnated with TiO_2 particles. This may be obtained by soaking the fabric or nonwoven with a suspension of TiO_2 particles, followed by a drying step. Depending on the thickness and size, the fabric or non woven may be used as such or mounted on a supporting frame to obtain a shaped photo-catalytic element of suitable rigidity, capable to keep its shape when placed in the refrigerator.

Some embodiments of the invention are now described with reference to the attached drawings, which illustrate the invention without limiting it, in which:

- Fig. 1 is a schematic perspective view of a first embodiment of a compartment of a refrigerator for storage of fruits and vegetables;
- Fig. 1A is a schematic top view of the cover of the compartment of Fig. 1;
- Fig. 1B is a schematic top view of the bottom of the compartment of Fig. 1;
- Fig. 1C is a schematic elevation view of a part of the compartment of Fig. 1;
- Fig. 1D is a schematic enlarged perspective view of a portion of the compartment of Fig. 1;
- Fig. 2 - Fig. 1 is a schematic perspective view of a second embodiment of a compartment of a refrigerator for storage of fruits and vegetables;
- Fig. 2A is a schematic top view of the cover of the compartment of Fig. 2;
- Fig. 2B is a schematic top view of the catalytic element of the compartment of Fig. 2;

- Fig. 2C is a schematic elevation view of a part of the compartment of Fig. 2;
- Fig. 2D is a schematic enlarged perspective view of a portion of the compartment of Fig. 2.

With reference to Figures 1-1D, a fruit and vegetable compartment, or crisper drawer, of a refrigerator is designated with 10. Such compartment is designed to be housed in a refrigerator (not shown), which typically comprises a refrigerating compartment, a freezing compartment, an evaporator located in the rear wall of the freezing compartment and other parts as known to the skilled person.

A crisper drawer consists thus essentially of a container 12 defining an inner chamber to store produce, open upwards and inserted in the refrigerator below an horizontal partition 14 forming a supporting plane for other products to be stored. Partition 14 forms also the cover of the crisper drawer or compartment.

A photo-catalytic element 16 is mounted within the inner chamber on the bottom 18 of the container 12. The photo-catalytic element 16 has the shape of a rectangular frame whose external size fits into the container 12, resting on the bottom 18 and extending along the peripheral portion of the bottom 18, so that the space within the rectangular frame forms a tray for storing produces 22. As mentioned above, in this embodiment the photo-catalytic element 16 comprises a polypropylene film 16a of a food packaging grade, coated with a layer 16b of titanium dioxide.

An array of UV lamps 20 are supported by partition 14, or cover of the crisper drawer. UV lamps 20 are mounted in cover 14 at positions vertically superimposed to the photo-catalytic element 16, namely they are placed near the perimeter of the cover 14. Such arrangement of UV lamps 20 directs the UV light emitted by the lamps toward corresponding portions of the photo-catalytic element 16, thereby

exerting a photo-catalytic activity on the conversion of ethylene and other VOC to carbon dioxide and water.

UV lamps 20 are preferably of the LED type. They form a lighting system that works preferably according to an on/off algorithm. The photo-catalyzed reaction does not involve only ethylene reduction but also an increase in carbon dioxide content, which leads to a delay/inhibition of ripening and senescence. As previously described, carbon dioxide has a bacteriostatic effect on aerobic bacteria and mould, and inhibits produce respiration. The photo-formed -OH species, as consequence of such process, also play a significant effect in microbial and odor control as a supplementary benefit of the ethylene molecule inactivation.

The algorithm controlling the lighting system can be combined with data from an infra-red gas sensor suitable to detect carbon dioxide in the compartment. To avoid fruits and vegetables acidification, carbon dioxide concentration should be kept below 10%. Since this gas is very soluble in water, if its concentration exceeds this threshold, undesired acidification can occur and fruit and vegetable tissue consistency and taste could be modified.

The ripening and senescence delay may thus not only be based on ethylene degradation but also on control of the carbon dioxide level. The smaller the compartment air gaps, the less frequently the lighting system needs to be activated, which helps reducing energy consumption. Also, in order to avoid temperature increase in the compartment, the lit phase is associated with the compressor-on phase. The sensor can be selected in such way to directly control ethylene concentration and indirectly monitor the carbon dioxide content.

Figures 2-2D show a second embodiment of a fruits and vegetables compartment according to the invention.

In this second embodiment the photo-catalytic element 30 is a fabric impregnated with TiO_2 particles mounted on a rigid frame 32, as described above. The frame is in turn slidably mounted on drawer rails 34 fixed to the walls of the drawer, below the cover 14.

In this embodiment the photo-catalytic element extends over the entire width of the container or drawer 12, so that the photo-catalytic action is exerted on a large surface of contact with the atmosphere of the drawer.

A lighting system comprising UV lamps 20 as described above is supported by the cover 14. The position of the UV lamps may be the same as described for the other embodiment, namely close to the perimeter of the cover 14, or it may be different, for example including lamps arranged also in the centre of the cover 14 (not shown).

The photo-catalytic element 30 is mounted close to the cover 14 supporting the lighting system (as shown in Figures 2 and 2D), the optimal distance being a function of the UV LED intensity.

The crisper drawer can be equipped with a fan to better force air through the fabric 30.

It is apparent that in both the embodiments described above the UV light emitted by the lamps 20 hits directly the photo-catalytic elements 16 or 30 without any other part of the compartment or refrigerator intercepting or filtering such light or generating shadows on the photo-catalytic element, which would reduce the catalytic action.

Also, carbon dioxide formed by the photo-catalytic conversion of ethylene is in direct contact with the produces contained in the compartment, and can effectively exerts its inhibitory action.

It is clear from the description above that other embodiments of the crisper drawer are possible within the same inventive concept.

CLAIMS

1. Compartment (10) of a refrigerator for storage of fruits and vegetables comprising a photo-catalytic element (16; 30) and a source of UV light (20), said compartment comprising a bottom (18) and an open upper part defining an inner chamber open upwards, said compartment being characterized in that:
 - said photo-catalytic element (16; 30) is housed on the bottom (18) of said inner chamber of said compartment or is mounted directly above said inner chamber, said photo-catalytic element (16) comprising at least a portion extending along or being superimposed to the peripheral portion of the bottom (18) of said chamber; and
 - said source of UV light (20) comprises a plurality of UV lamps arranged above said photo-catalytic element (16; 30), so that the UV light emitted by said lamps hits directly said photo-catalytic element.
2. Compartment (10) of a refrigerator according to claim 1, characterized in that said photo-catalytic element (16; 30) comprises particles of titanium dioxide.
3. Compartment (10) of a refrigerator according to claim 2, characterized in that said photo-catalytic element (16; 30) comprises an amount of TiO₂ particles of from 2 to 30% by weight, preferably from 5 to 20% by weight, more preferably from 8 to 15% by weight.
4. Compartment (10) of a refrigerator according to claim 2, characterized in that said photo-catalytic element (16; 30) comprises TiO₂ particles having an average size of from 0.1 to 20 µm, preferably from 0.5 to 15 µm, more preferably from 1 to 10 µm.
5. Compartment (10) of a refrigerator according to claim 2, characterized in that

said photo-catalytic element (16; 30) comprises TiO_2 particles in the anatase polymorphic form.

6. Compartment (10) of a refrigerator according to any of claims 1-5, characterized in that said photo-catalytic element has the shape of a rectangular frame (16) whose external size fits into said compartment (10) and extends along the peripheral portion of said compartment.
7. Compartment (10) of a refrigerator according to claim 6, characterized in that said photo-catalytic element (16) having the shape of a rectangular frame rests on the bottom (18) of said compartment.
8. Compartment (10) of a refrigerator according to claim 6, characterized in that said photo-catalytic element (16) comprises a support (16a) coated with a layer (16b) of particles of titanium dioxide.
9. Compartment (10) of a refrigerator according to any claims 1-5, characterized in that said photo-catalytic element (30) is a fabric or nonwoven impregnated with TiO_2 particles mounted on a rigid frame (32) slidably mounted on drawer rails (34) fixed to the walls of said compartment below said cover (14).
10. Compartment (10) of a refrigerator according to claim 9, characterized in that said fabric or nonwoven extends over the entire width of said compartment or drawer (12).
11. Compartment (10) of a refrigerator according to claim 1, characterized in that said plurality of UV lamps (20) are supported by a partition (14) of said compartment.
12. Compartment (10) of a refrigerator according to claim 10, characterized in that said plurality of UV lamps (20) are of the LED type.
13. Compartment (10) of a refrigerator according to claim 11 or 12, characterized

in that said plurality of UV lamps (20) are operated according to an on/off algorithm which takes into account also data from an infra-red gas sensor suitable to detect the amount of carbon dioxide in said compartment, whereby carbon dioxide concentration is controlled.

14. Compartment (10) of a refrigerator according to claim 13, characterized in that said concentration of carbon dioxide is kept below 10% by weight.

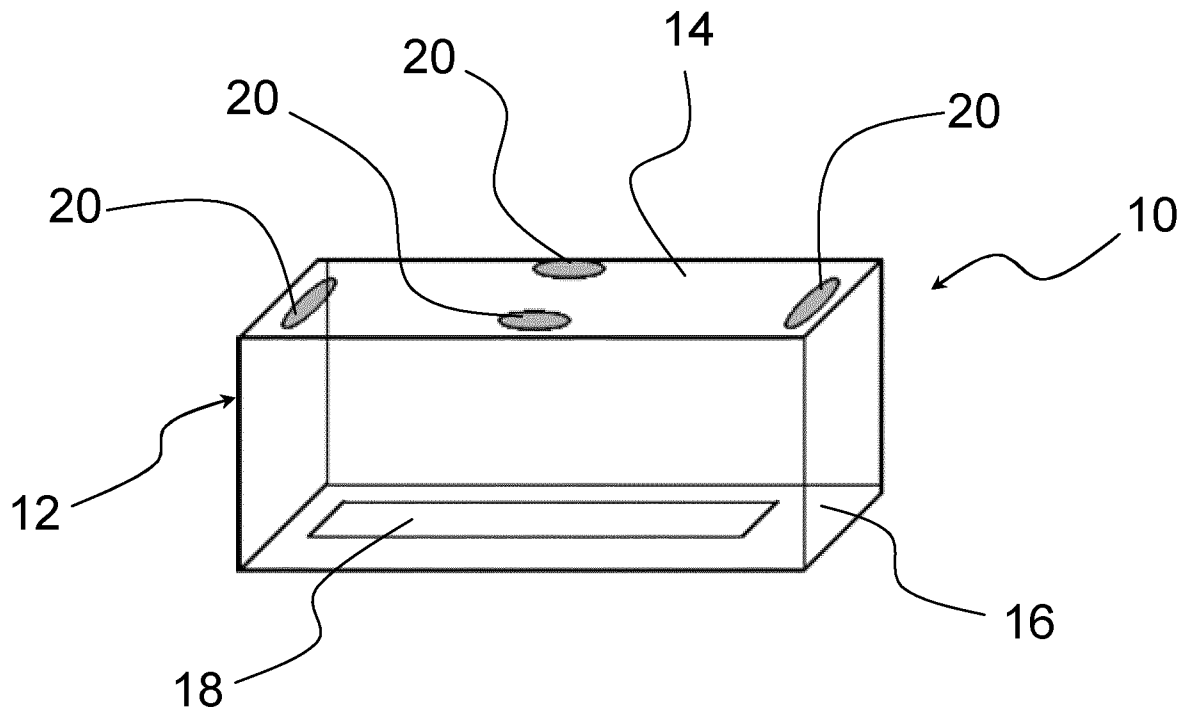


Fig. 1

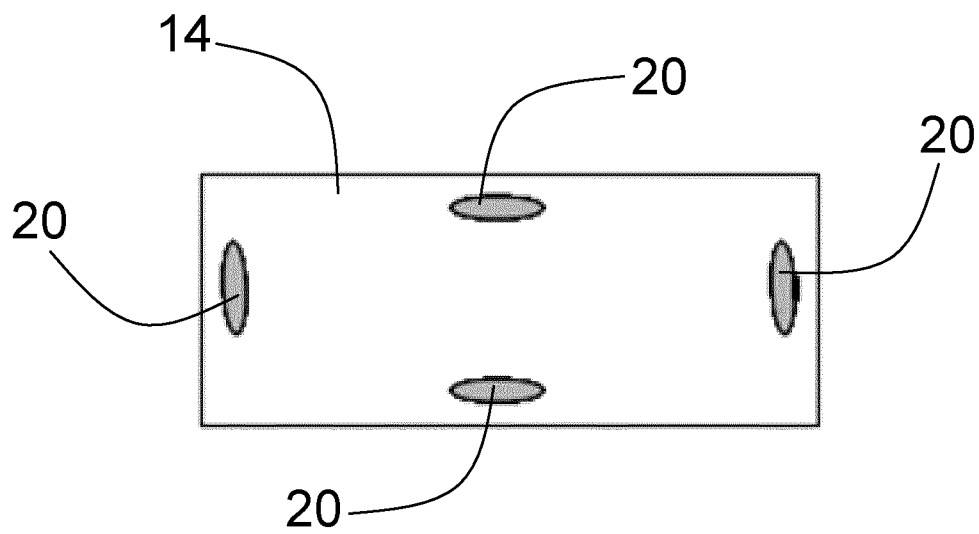


Fig. 1A

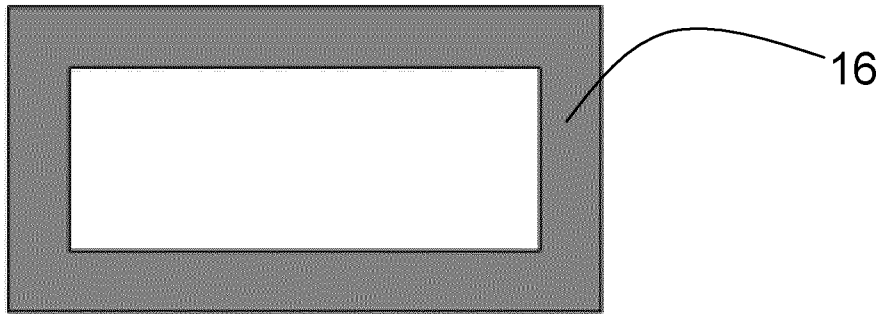


Fig 1B

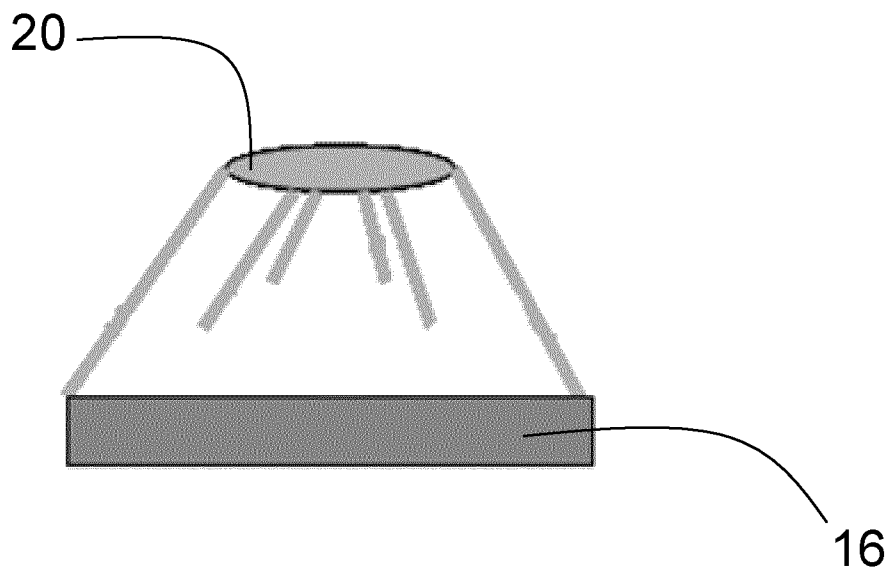


Fig. 1C

3/5

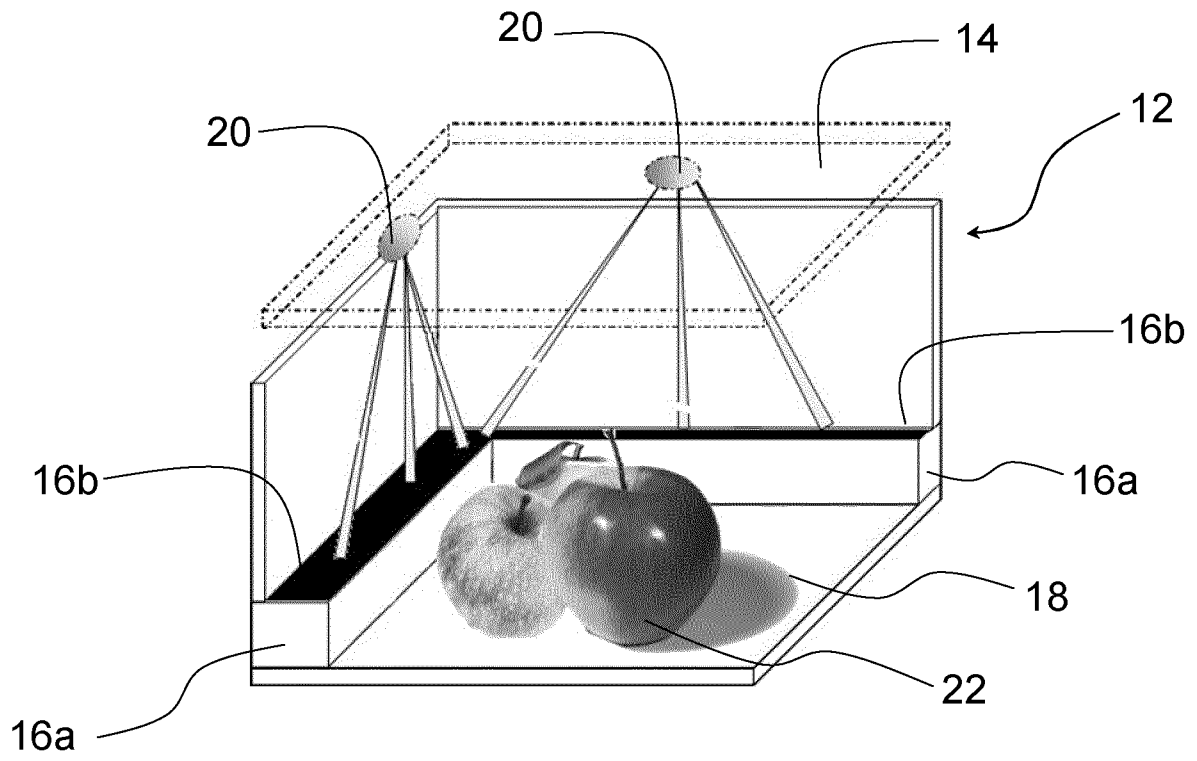


Fig. 1D

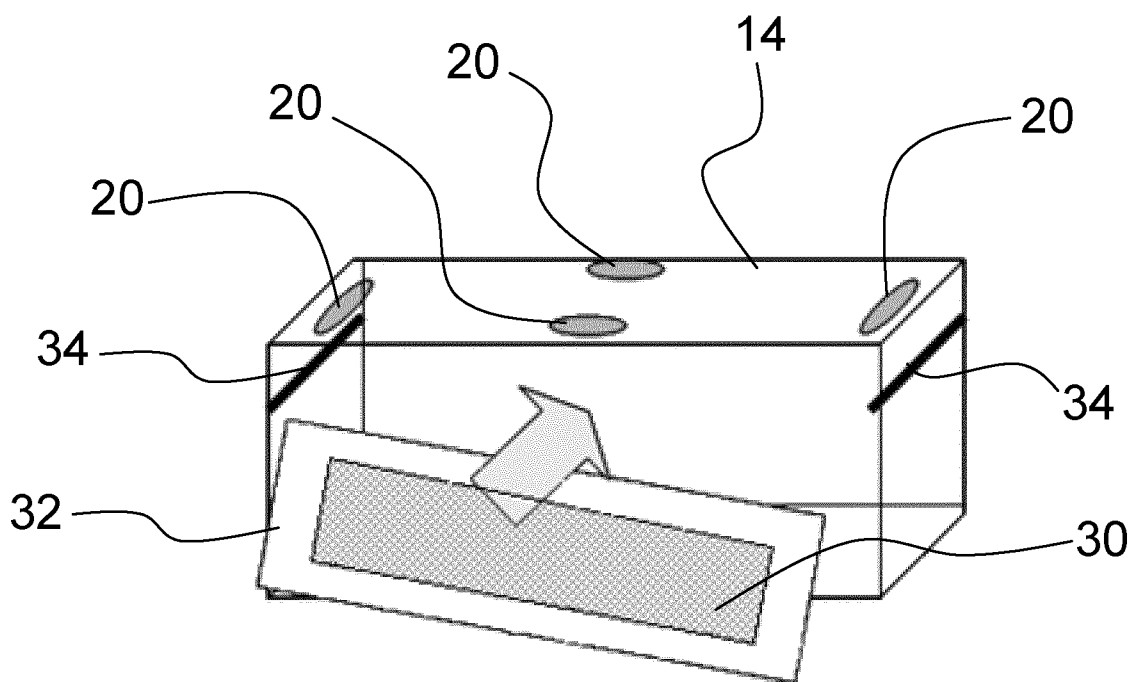


Fig. 2

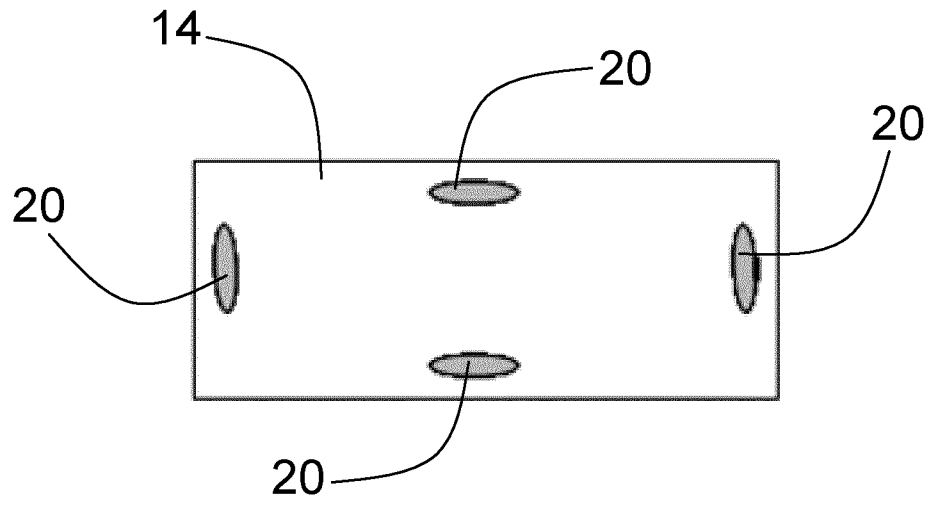


Fig. 2A

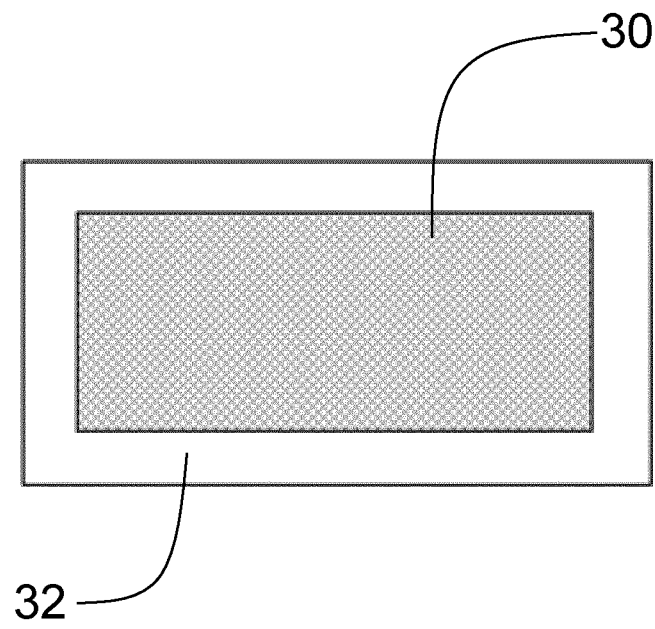
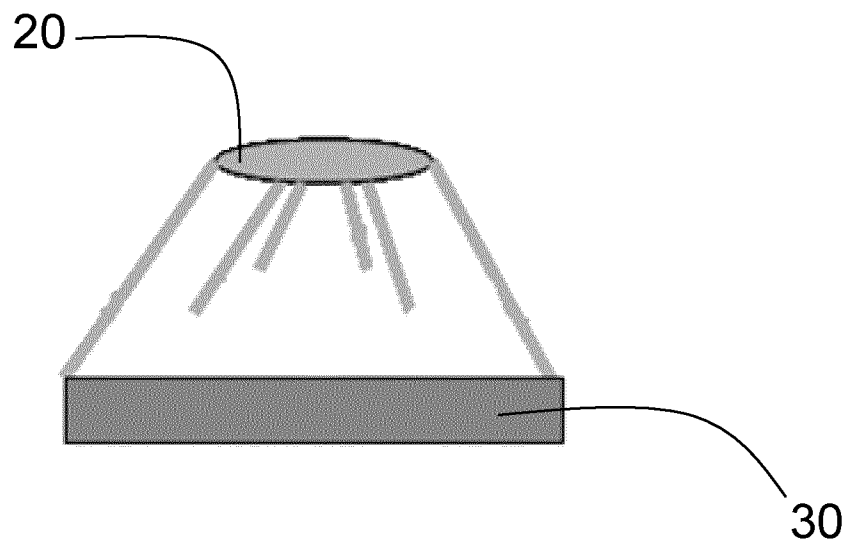
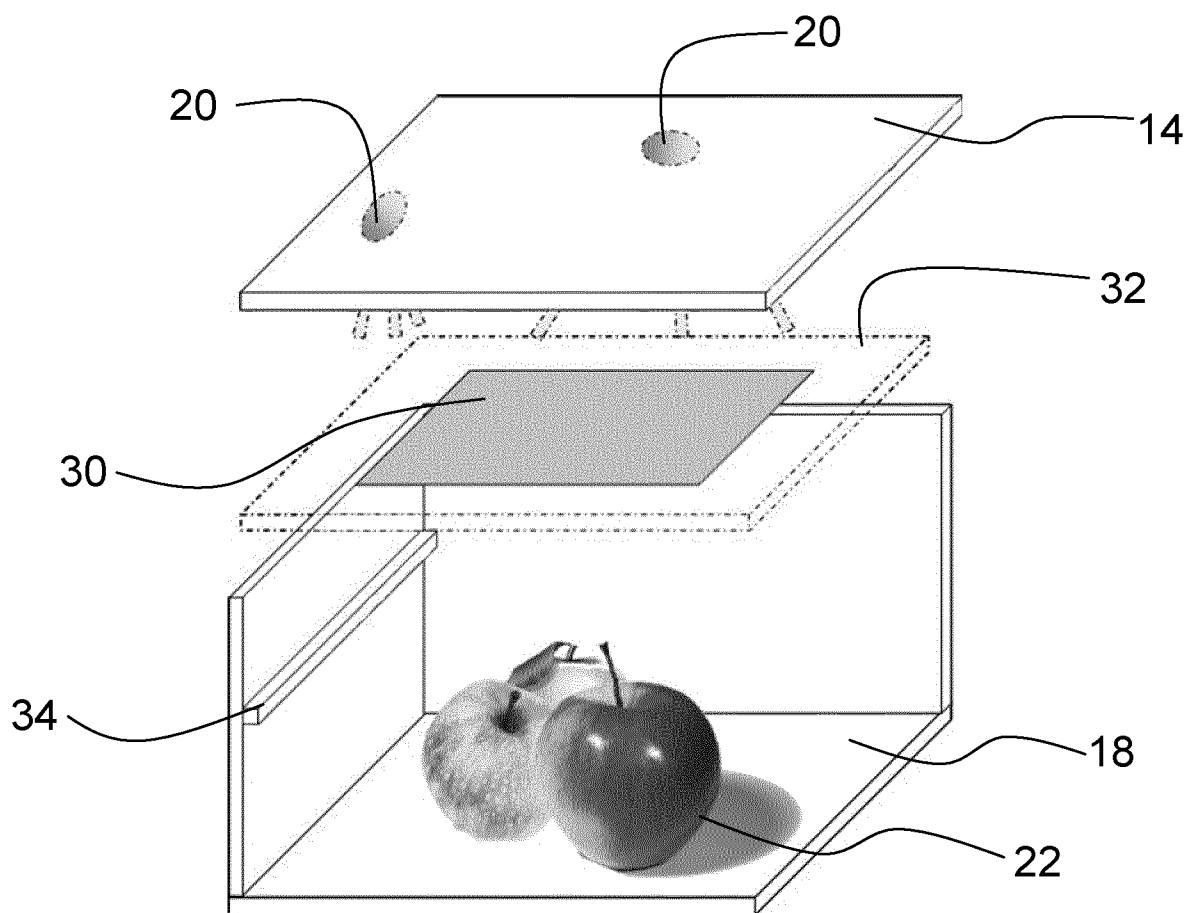


Fig. 2B

**Fig. 2C****Fig. 2D**

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/055778

A. CLASSIFICATION OF SUBJECT MATTER
INV. F25D17/04
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)
F25D

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 2007/049937 A2 (LG ELECTRONICS INC [KR]; MIN DEUL RE [KR]; KIM EUN JEONG [KR]; SHIN JO) 3 May 2007 (2007-05-03) figures 1-22 -----	1-14
A	JP 2002 333266 A (MATSUSHITA REFRIGERATION) 22 November 2002 (2002-11-22) paragraph [0041] -----	5
A	EP 2 141 427 A1 (PANASONIC CORP [JP]) 6 January 2010 (2010-01-06) paragraph [0497] -----	9
X	WO 2007/072165 A2 (INDESIT CO SPA [IT]; FARALDI PAOLO [IT]; POLVERINI DAVIDE [IT]; FIORET) 28 June 2007 (2007-06-28) figure 1 -----	1,2,6-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

21 May 2012

Date of mailing of the international search report

06/06/2012

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

Dezso, Gabor

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/055778

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007049937 A2	03-05-2007	AU 2006306845 A1 EP 1949010 A2 US 2008307818 A1 WO 2007049937 A2	03-05-2007 30-07-2008 18-12-2008 03-05-2007
JP 2002333266 A	22-11-2002	NONE	
EP 2141427 A1	06-01-2010	EP 2141427 A1 TW 200912226 A WO 2008132817 A1	06-01-2010 16-03-2009 06-11-2008
WO 2007072165 A2	28-06-2007	IT T020050180 U1 WO 2007072165 A2	20-06-2007 28-06-2007