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(71) Applicant (for all designated States except US): **SECURIS LIMITED** [GB/GB]; Garrett House, 24 Windmill Road, Brentford, Middlesex TW8 0QA (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MACHNICKI, Andrew** [GB/GB]; c/o Securis Limited, Garrett House, 24 Windmill Road, Brentford, Middlesex TW8 0QA (GB).

(74) Agent: **WHITE, Nicholas**; Rouse Patents, Windsor House, Cornwall Road, Harrogate HG1 2PW (GB).

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(54) Title: FILM HAVING OPTICALLY VARIABLE EFFECT STRUCTURE

(57) Abstract: A shrinkable film element is provided which consists of a shrinkable film with an optically variable effect on the external surface of the film and imaged regions and/or indicia on the internal surface of the film. The film in the form of a shrink wrap sleeve provides for a stable better quality image after heat shrinking onto an object. The images and indicia may be easily observed and are stable and the optically variable effect is less susceptible to post heat shrinking degradation and loss of image quality.



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FILM HAVING OPTICALLY VARIABLE EFFECT STRUCTURE

[0001] The present invention relates to shrinkable film elements incorporating optically variable effects, to methods of manufacturing shrinkable
5 film elements incorporating optically variable effects and to their use.

[0002] Optically variable effect structures such as holograms and diffraction gratings have been used widely in recent years to impart security to documents of value such as banknotes, credit cards and the like. Shrinkable
10 films in the form of wraps have seen a wide variety of applications such as CD overwraps, bottle wraps, beverage container wrappings, labels for packaging, especially food packaging, and sealing bands used in tamper evident applications.

[0003] Optically variable effect structures have been imparted to films e.g. shrinkable films in a variety of ways. For example, materials are typically rendered holographic via a process of micro-embossing at elevated temperatures and pressures. Such processes are described in U.S. Pat. Nos. 4,913,858; 5,164,227; 5,503,792; 5,155,604; and 5,662,986; substrates are
20 rendered holographic under high heat and pressure. Because shrink wrap films are engineered to shrink under heat, it is not possible to emboss such films using traditional techniques.

[0004] It is also known to impart films with a micro-embossed structure during an extrusion and casting processes, such as described, for example, in
25 U.S. Pat. Nos. 5,003,915; 4,913,858; 5,164,221; 5,155,604 and 5,182,069. The disadvantages of such routes include the need for capital equipment such as extruders and, in the latter case, the depth of embossing (up to two orders of magnitude deeper) which can be better described as macro-embossing.

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[0005] It is also known to render materials holographic via a transfer process as taught in U.S. Pat. Nos. 5,383,687 and 5,662,996. Both inventions

therein utilize heat and pressure to achieve their ends and focus on aluminum metalized transfers. In both inventions, the heat required is well beyond the temperatures at which the shrink wrap film will begin to contract, rendering such approaches in the context of shrink wrap films inappropriate.

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[0006] More recently, techniques such as insitu polymerization replication (ISPR) have been developed in which a polymer or resin is cast or molded against a holographic or other optically variable effect profile continuously while the polymer is held on a substrate, the profile then being retained by curing on or after removal from the profiled mould. Examples of this approach are described in US-A-3689346, US-A-4758296, US-A-4840757, US-A-4933120, USA-5003915, US-A-5085514 and DE-A-4132476. In many of these examples, the optically variable effect structure is formed on a carrier for subsequent transfer although in some cases the structure is formed directly on the end product substrate.

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[0007] Recently ISPR techniques have been used to impart optical variable effects on shrinkable film elements. In U.S. Pat. Publication No. 2005/0012970 a holographic shrink wrap element and its process of manufacture is described. The holographic image is imprinted from a polymer film into the surface of an electron-beam curable adhesive deposited on the surface of a shrink wrap film; the holographic image being exposed on removal of the polymer film. In U.S. Pat. Publication No. 2004/0188871 a holographic image shrinkable film is prepared using a UV curable resin and an embossing roller. Published international patent application WO 99/38704 discloses a security device based on shrinkable substrate, which incorporates an optically variable effect structure derived from a radiation curable material. In this published application, when security is deemed critical, the optically variable effect structure derived from radiation curable material is located on the interior surface of the device with an optional adhesive layer over the optically variable effect. It is envisaged that indicia, optionally in the form of windows, may be printed on the opposite surface that is the exterior surface, of the device. It is

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also envisaged that when high security is not critical that the optically variable effect may be provided on the exterior surface of the device, that is on the same side as the indicia. There have been a number of problems associated with such devices. The first problem is that after heat shrinking operations using steam or hot water the holographic images derived from the radiation curable material and located on the inside of the device may be damaged due to the entrapment of water proximate to the holographic image. Furthermore it has been difficult to achieve good quality holographic images in such arrangements that provide a good optical effect. Also problematic has been the damage that may be caused to the high refractive index coatings often used with holographic images to enhance their appearance. A further problem is that these devices have limited application due to the limiting effects of these technical problems.

[0008] In an increasingly competitive marketplace, shrinkable film elements are being called upon to provide more functionality including packaging design and security, primarily due to the difficulty in forging holograms. Heretofore, shrinkable film elements have not been available with holographic patterns, which are able to provide strong eye appeal and security simultaneously. In the present invention the shrinkable film element may be referred to as shrink wrap element containing a shrink wrap film, which is also known as "heat shrink film" or "shrink film". There is a need therefore for shrinkable film elements that are able to combine the benefits of printed indicia and/or layers with optically variable effects derived from radiation curable materials which are stable under the conditions of and after shrinking operations and produce bright and optically acceptable images after the shrinking operations.

[0009] The present invention therefore provides a shrinkable film element comprising an optically variable effect derived from a radiation curable material located on the external surface of a shrinkable substrate and imaged regions and/or indicia on the internal surface of the substrate.

[0010] The present invention is also directed to a process for the preparation of a shrinkable film element. This in accordance with the present invention there is provided a method for the manufacture of a shrinkable film element, which method comprises forming an optically variable effect derived
5 from a radiation curable material on the exterior of a shrinkable substrate by providing a radiation curable material on the external surface of the shrinkable substrate; imparting an optically variable effect structure on or into the radiation curable material; and then curing of the material so that it retains the optically variable effect structure and either before or after formation of the optically
10 variable effect structure imparting imaged regions and/or indicia onto the internal surface of the substrate.

[0011] It is preferred that the shrinkable film element is in the form of a sleeve, with the optically variable element being located on the exterior surface
15 of the sleeve.

[0012] The process can be a web based process and can be operated at high speeds, for example up to 300 meters/minute or more while providing high fidelity, stable structures in the final shrinkable film element.

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[0013] The present invention also provides for a method of applying a shrinkable film element to an object. Which process comprises inserting the object into the shrinkable film element in the form of a sleeve or wrap and in the pre-shrunk state and shrinking the shrinkable film element by the action of heat
25 and/or chemicals and/or steam such that the shrinkable element shrinks and engages with the object such that the imaged regions and/or indicia are in contact with the object and may be viewed through the shrunken substrate.

[0014] Most conventional heat shrinkable materials can be used for the shrinkable substrate of the shrinkable film element, typically polymer films which
30 have been bi-axially oriented. The film can be any suitable polymer material for example poly(vinyl chloride), poly(propylene), poly(ethylene), poly(ethylene

terephthalate) or other polyester, poly(acrylates), poly(vinylidene chloride) or poly(styrene) e.g. orientated poly(styrene). Copolymers of the foregoing may also be used. It is preferred that the polymeric material be a transparent poly(propylene), PVC, or polyester film. The shrinkable substrate used in this invention is generally a commercially available non-holographic shrink wrap film such as those shrink film materials sold under the trade mark REYNOLON[®] by Alcoa or the trade mark CLYSAR[®] by The Bermis Company or those sold under the trade mark Propafilm[™] by Innovia films or those sold under the trade mark Mylar[®] by DuPont Teijin Films.

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[0015] The film thickness is preferably within the range from 12.5 to 150 μm , preferably 40 to 100 μm , more preferably 40 to 80 μm . Preferably the film has a percent shrinkage between five and 80%, in the TD direction, preferably 20 and 75%, more preferably 50 to 75%, as measured by ASTM D955 10 seconds at 90°C. In one embodiment it is preferred that the shrinkage is less than 15%. Mono-axially orientated films have typical shrink characteristics of up to 80% in the transverse direction (TD) and up to 10% in the machine direction (MD). It is preferred that the film has an MD shrinkage of less than 7%, preferably less than 5% and most preferably less than 2% at 10 seconds in water at 90°C. Preferably the elongation at break (ASTM D882-83) in the MD direction is between 120 and 500%, more preferably between 120 and 450%, more preferably between 200 and 425% more preferably between 300 and 425%. Preferably the elongation at break (ASTM D882-83) in the TD direction is between 40 and 200% preferably 50 and 120%.

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[0016] Their surfaces of these films will vary and different curing formulations will be needed as appropriate together with different surface treatments or primers.

30 **[0017]** The radiation curable composition used for the shrinkable film element may be a composition that is one of three types. The first are free radical polymerized or cured resin systems which are unsaturated resins or

- monomers, pre-polymers, oligomers etc that contain vinyl and/or acrylate unsaturation for example and which polymerize and/or cross-link through use of a photo initiator activated by the radiation source employed e.g. UV. These are typically referred to as radical systems. The second is cationic polymerizable or cured resins in which ring opening (e.g. epoxy rings) is effected using photoinitiators or catalysts which generate ionic entities under the radiation source employed e.g. UV. The ring opening is followed by cationic polymerization and/or intermolecular cross-linking. Also used as cationically curable systems are resins that contain one or more groups with vinyl unsaturation. These systems are typically referred to as cationic systems. The third type is a hybrid cured systems in which both free radical cured resins and cationic cured resins are combined. These systems are typically referred to as radical/cationic systems or combined systems.
- [0018]** Detailed descriptions of the chemistries and formulations that may be used in radical, cationic and hybrid systems are described for example in the following references: United States Letters Patent No. 3,794,576; Crivello et. al. in Journal of Radiation Curing, Vol. 4, page 2 (1977); Crivello et. al. in Journal of Radiation Curing, Vol. 5, page 2 (January 1978); United States Letters Patent No. 4,090,936; United States Letters Patent No. 4,069,055; United States Letters Patent No. 4,058,401. "UV Curing: Science and Technology" edited by S. P. Pappas, Technology Marketing Corporation, Stamford, Connecticut; "Radiation Curing of Coatings", J.V. Koleske, Astm Intl, April 2002; "Cationic Radiation Curing", Joseph V. Koleske, June 1991; "Photoinitiation for Polymerization: UV & EB at the Millenium", D. C. Neckers, John Wiley & Sons, June 1999; "Radiation Curing in Polymer Science and Technology: Fundamentals and Methods", J.P. Fouassier; "Radiation Curing in Polymer Science and Technology: Polymerization Mechanisms", J.F. Rabek, Kluwer Academic Print, March 1993; "Radiation Curing in Polymer Science and Technology: Polymerization Mechanisms", J.F. Rabek, Kluwer Academic Pub, January 1994; "Radiation Curing in Polymer Science and Technology: Practical Aspects and Applications", J.F. Rabek, Kluwer Academic, March 1993;

"Radiation Curing in Polymer Science & Technology: Photoinitiating Systems, Vol. 2", J.P. P. Fouassier, J.F. Rabek, March 1993.

5 **[0019]** Typical resins useful UV curable resins are styreneated polyesters and acrylics, such as vinyl copolymers of various monomers and glycidyl methacrylate reacted with acrylic acid, isocyanate prepolymers reacted with an hydroxyalkyl acrylate, epoxy resins reacted with acrylic or methacrylic acid, and hydroxyalkyl acrylate reacted with an anhydride and subsequently reacted with an epoxy.

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15 **[0020]** The radiation used to effect curing of the radiation curable composition will typically be UV radiation, alternatively or in combination the radiation source could include electron beam, visible, infra-red or higher wavelength radiation, depending upon the material, its absorbance and the process used.

20 **[0021]** An important aspect of these resins is that they can be cured at modest (less than 70°C) or even ambient temperature while operating at realistic production speed and therefore reduce the risk of damage to the structure by avoiding local overheating attack or stress. They can also be used as thin layers and provide efficient conversion of radiation energy to heat. The low temperature of operation is also vital for curing the resin systems when in contact with heat shrinkable film.

25 **[0022]** The shrinkable substrate material will be transparent or translucent and may be tinted, such that the imaged regions and/or indicia may be viewed through the material. In some embodiments the imaged region constitutes a substantially complete covering of the internal surface of the shrinkable element with a printed ink e.g. process colour ink image or a
30 metalized coating. This printed layer imparting a colour through the material when viewed from the exterior surface. It is preferred that the inks used are gravure or flexographic inks. Preferably the inks are formulated to exhibit a

capacity for considerable and commensurate shrinkage to that of the shrinkable film when dried onto the shrinkable film and exposed to the conditions used to shrink the heat shrinkable element. Preferably the ink is a water based flexographic ink. The inks may be UV curable flexographic inks. In a preferred embodiment the radiation curable material is formulated to provide a holographic image that is heat shrinkable and which has the capacity to shrink by an amount that is commensurate with that of the shrinkable film. Examples of suitable UV curable flexographic inks include those sold under the trade mark Spectrum™ and Fidelity™ by Sun Chemical Company.

[0023] The optically variable effect may be a hologram or diffraction grating and is preferably applied in the direction of least shrinkage of the substrate. This assists in preserving the form of the structure and optical replay after heat shrinking has been carried out. (The hologram or diffraction grating will preferably be viewable under white light illumination but could also be viewable under non white light e.g. V or IR.) The direction of least film shrinkage will be dependent on the manner in which the film or substrate has been manufactured. Shrinkage films are made by stretching the base material and orienting the molecules. The resultant products may then shrink on thermal or chemical exposure by 55-70% across the film and 5-7% in the linear direction. Depending on the article and the shrink required we would normally apply the images so that the replay would be in the linear direction i.e. least shrink effects.

[0024] Typically, the structure will be compressed on heat shrinkage by about 5% and thus must be resilient so that it will retain its integrity. Stress from heat and shrinkage must not destroy or significantly reduce the image replay or cause loss of adhesion, mechanical stress, cracking, etc.

[0025] With some substrates such as PVC, retention of the integrity of the structure will occur without further action being required. In other cases, however, such as on PET substrates, a pre-treatment may be required to

achieve bonding, colouring or other effects or mechanical stress relief layers. This priming or pre-treatment may involve corona treatment with or without a thin layer coating before ISPR or a suitable thin layer directly applied to the substrate material. Corona discharge treatment will clean the surface and
5 improve its wetting and bonding capacity to a primer layer or to the ISPR (or radiation curable) layer often without the use of a separate thin primer layer.

[0026] The optically variable effect may further comprise a high reflective layer, such as a metallization or a high refractive index material, over its
10 surface. This promotes the replay of the optically variable effect but will not always be necessary particularly if subtle effects are required. If a metallization is provided, this may be partially demetalised to achieve a patterning effect while a further protective lacquer could be applied over the optically variable effect generating structure either before or after curing.

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[0027] In a further option, an adhesive layer could be provided over the imaged region or indicia, which enables the shrinkable film element to be adhered to an article. This is particularly useful where the finished product is to be used in the form of a shrink sleeve or the like.

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[0028] The surface relief structure which generates the optically variable effect could be a Kinegraphic effect or an holographic effect generating structure which is intended to include also all types of white light diffracting surface relief patterns formed in a polymeric medium in which the patterned
25 surface is reflectively or refractively coated with an image enhancing composition such as a thin layer of aluminium or one or a number of stacked layers of zinc sulphide. Such coatings and equivalents are well known in the art and examples may be found in EP 201323A. The aluminium or other films could be provided in a continuous form or fine halftone dot formation as
30 described in EP 328086A. The image intensifying layer may be any reflective or high index material. For example, the image intensifying layer may be at least one of the following: a vacuum vapor deposited aluminum; silicon monoxide;

silicon dioxide; aluminum oxide; magnesium fluoride; zinc sulfide; titanium dioxide; tin tungsten oxide and indium tin oxide. Of these, the vacuum vapor deposited aluminum is preferred. Typical coating thicknesses for the image intensifying layer are 200-400 . The image intensifying layer is optionally
5 present with the release coating.

[0029] The visual appearance resulting from such diffracting structures may thus be of a regular diffraction grating, a mosaic of diffracting gratings, a three dimensional holographic spatial effect image or the like. Such diffracting
10 structures can be generated by holographic recording or electron beam generation. For example, the optically variable effect generating structure may generate an holographic effect at least in one visually identifiable area, the structure being formed by a fine surface profile formed in a transparent plastic film, the profile being reflectively coated.

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[0030] In some cases, particularly for substrate materials such as polypropylene and polyethylene, the UV curable resin may not adhere sufficiently strongly. To improve this, a primer could be applied to the substrate prior to coating the resin. Also, a corona treatment at for example 38-44
20 dynes/cm could be used to increase surface bonding. Suitable primers are known in the art.

[0031] Once the shrinkable film has been provided with an optically variable effect on its exterior and imaged regions and/or indicia formed on its
25 interior the film may be formed into a shrink sleeve which will then be placed around an article to be protected, the sleeve then being shrunk onto the article in a conventional manner, usually by heat. If an adhesive is provided then the sleeve will additionally adhere to the article. This provides a very secure tamper evident security item.

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[0032] The method of forming the optically variable effect from radiation curable materials may be carried out in accordance with the procedures

described in U.S. Pat. Publication No. 2005/0012970, U.S. Pat. Publication No. 2004/0188871, WO 99/38704 and WO 94/18609, the contents of each being hereby incorporated by reference.

- 5 **[0033]** Generally the procedure involves applying an ink coating to what will be used as the interior surface of the shrinkable film via flexographic or gravure printing/coating techniques. Drying of the ink coating or if used individual regions and/or indicia. Then on the opposite external surface a UV curable resin is applied to a thickness of 0.1 to 10 um preferably 1-7 um, and
- 10 more preferably 1 to 5 um, preferably by using off-set printing or gravure printing. Then the UV resin is forced against a metal wheel engraved with a holographic pattern to impart the resin with the image. The resin is then illuminated with UV radiation to harden the resin.
- 15 **[0034]** The invention therefore provides a shrinkable film element is provided which consists of a shrinkable film with an optically variable effect on the external surface of the film and imaged regions and/or indicia on the internal surface of the film. The film in the form of a shrink wrap sleeve provides for a stable better quality image after heat shrinking onto an object. The images and
- 20 indicia may be easily observed and are stable and the optically variable effect is less susceptible to post heat shrinking degradation and loss of image quality.

- [0035]** It is noted that the shrinkable film element and the manufacture thereof described above is the preferred embodiment of the present invention
- 25 for the purpose of illustration only, and are not intended as a definition of the limits and scope of the invention disclosed. Any modifications and variations that maybe apparent to a person skilled in the art are intended to be included within the scope of the present invention.

CLAIMS

1. A shrinkable film element comprising an optically variable effect derived from a radiation curable material located on the external surface of a shrinkable substrate and imaged regions and/or indicia on the internal surface of the substrate.
2. A shrinkable film element as claimed in claim 1 in the form of a sleeve.
3. A shrinkable film element as claimed in claim 1 or claim 2 wherein the shrinkable substrate is a heat shrinkable polyester.
4. A shrinkable film element as claimed in any one of the preceding claims wherein the radiation curable material is UV curable.
5. A shrinkable film element as claimed in any one of the preceding claims wherein the imaged regions and/or indicia are provided by printing.
6. A shrinkable film element as claimed in claim 5 wherein the printing method is flexographic and/or gravure.
7. A method for the manufacture of a shrinkable film element, which method comprises forming an optically variable effect derived from a radiation curable material on the exterior of a shrinkable substrate by providing a radiation curable material on the external surface of the shrinkable substrate; imparting an optically variable effect structure on or into the radiation curable material; and then curing of the material so that it retains the optically variable effect structure and either before or after formation of the optically variable effect structure imparting imaged regions and/or indicia onto the internal surface of the substrate.

8. A method of applying a shrinkable film element to an object, which method comprises inserting the object into the shrinkable film element in the pre-shrunk state in the form of a sleeve or wrap and shrinking the shrinkable film element by the action of heat and/or chemicals and/or steam such that the shrinkable element shrinks and engages with the object such that the imaged regions and/or indicia are in contact with the object and may be viewed through the shrunken substrate.
9. An object comprising a shrinkable film element in the shrunken state and having imaged regions and/or indicia on the internal surface of the shrinkable element in contact with the object and viewable through the substrate and an optically variable effect derived from a radiation curable material on the external surface of the shrinkable film element.
10. An element method or object as claimed in any one of the preceding claims, wherein the shrinkable substrate comprises a bi-axially oriented polymer film.
11. An element method or object according to any of the preceding claims, wherein the shrinkable substrate is transparent.
12. An element method or object according to any of the preceding claims, wherein the optically variable effect structure generates a hologram or diffraction grating.
13. An element method or object according to any of the preceding claims, wherein the optically variable effect structure is applied in the direction of least shrinkage of the substrate.
14. An element method or object according to any of the preceding claims, further comprising providing a reflective layer on the optically variable effect structure.

15. An element method or object as claimed in claim 14, wherein said reflective or image intensifying layer comprises at least one member selected from the group consisting of vacuum vapor deposited aluminum, silicon monoxide, silicon dioxide, aluminum oxide, magnesium fluoride,
5 zinc sulfide, titanium dioxide, tin tungsten oxide and indium tin oxide.
16. The process of claim 22 further comprising providing a tie coat between said image intensifying layer and said cold laminating adhesive.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B41M3/00 B41M5/50

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)
B41M G03H B29D B29C B32B B44F B65D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, 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 99/38704 A (DE LA RUE INTERNATIONAL LIMITED) 5 August 1999 (1999-08-05) cited in the application claims 1,2,5,7,8,10,12,14 page 1, line 32 - line 37 page 2, line 7 page 3, line 27 - line 34 page 4, line 31 - page 5, line 13 page 5, line 34 - page 7, line 13 page 7, line 21 - line 25 page 8, line 20 - line 22 figures 1A-1E, 2A-2E	1-16
A	US 2004/188871 A1 (TSUNG-MING SHIAO ET AL.) 30 September 2004 (2004-09-30) cited in the application claims 1-8; figures 1-3 paragraph [0018]	1-16
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Bacon, A

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/012970 A1 (J.E.COX ET AL.) 20 January 2005 (2005-01-20) cited in the application paragraphs [0001], [0007], [0008] claims 13,16-18; figure 1 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/003701

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9938704	A	05-08-1999	AU 2066399 A 16-08-1999
		EP 1051301 A1 15-11-2000	
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US 2004188871	A1	30-09-2004	NONE
US 2005012970	A1	20-01-2005	NONE